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Addition reactions of η^3-allenyl/propargyl and η^3-trimethylenemethane complexes of platinum and palladium

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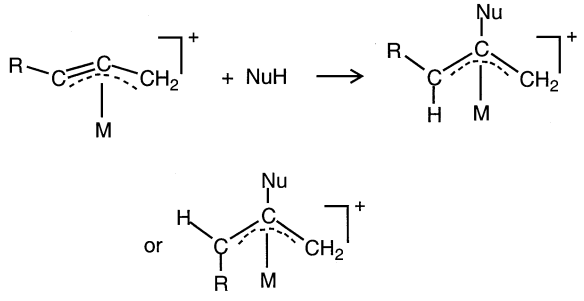
Abstract

A study of reactions of η^3-allenyl/propargyl complexes of platinum and palladium with transition-metal hydrides and secondary amines and of η^3-trimethylenemethane (η^3-TMM) complexes of platinum with unsaturated electrophiles is presented. The reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (**1a**OTf) with $Cp(CO)_2RuH$ affords the η^3-allyl complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHC(Ph)Ru(CO)_2\text{-}Cp)]OTf$, whereas that of **1a**OTf with $Cp_2Zr(Cl)H$ furnishes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCHPh)]OTf$ (**3**OTf). The source of the C*H*Ph hydrogen in the latter reaction appears to be adventitious H_2O, as evidenced by the formation of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCDPh)]OTf$ when **1a**OTf was treated with D_2O and $Cp_2Zr(Cl)H$. Possible mechanisms of formation of **3**OTf are presented. The secondary amines R_2NH (R = *i*-Pr or *sec*-Bu) react with **1a**OTs and its palladium analog, **1b**OTs, to give the η^3-(2-aminoallyl) complexes $[(PPh_3)_2M(\eta^3\text{-}CH_2C(NR_2)CHPh)]OTs$ (M = Pt, Pd). Competition studies reveal the following order of reactivity, attributed to steric effects: Et_2NH (74 and 38) > $(i\text{-}Pr)_2NH$ (3.5 and 5) > $(sec\text{-}Bu)_2NH$ (1) for **1a**OTs and **1b**OTs, respectively. The complex **1a**OTs reacts much faster with Et_2NH than with EtOH. Reactions of the η^3-TMM complexes $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2\text{-}Me)_2)CHR)$ (R = Me (**7**), Ph (**8**)) with the very strong electrophiles/polarophiles TCNE and *p*-toluenesulfonyl isocyanate (TSI) lead to [3+2] cycloaddition of the electrophile to the η^3-TMM ligand, and the resulting cycloadduct is isolated either free (with TSI) or complexed as an alkene to the metal (with TCNE). The weaker electrophiles diethyl fumarate and fumaronitrile (E) react with **7** or **8** to furnish $(PPh_3)_2PtE$ and a [3+3] coupling product of the η^3-TMM ligand. All new compounds were characterized by a combination of elemental analysis, mass spectrometry and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy.

Keywords: Platinum complexes; Palladium complexes; η^3-Allenyl/propargyl; η^3-Trimethylenemethane; Nucleophilic addition; Cycloaddition

1. Introduction

Cationic transition-metal η^3-allenyl/propargyl complexes react with a variety of nucleophilic reagents [1–6]. Generally, these reactions proceeded by addition of the nucleophile to the central carbon atom of the hydrocarbyl ligand as shown in Eq. (1), and a number of oxygen, nitrogen and carbon nucleophiles NuH, in particular, engage in such processes.



(1)

We [1,5] and another group [2] have been investigating addition reactions of nucleophiles with $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCR)]^+$ (R = H, Me, Ph) over the past several years, and these studies have been recently reviewed. In the present and the last paper in this series, we report further studies of addition of amines to $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (**1a**) and $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCPh)]^+$

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(**1b**) [7–9], as well as new investigations on analogous additions of transition-metal hydrido complexes to **1a**. Also included are cycloaddition reactions of the η^3-trimethylenemethane complexes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHR)]$ (R = Me (**7**), Ph (**8**)) with unsaturated electrophilic reagents, which expand on our previously published investigations [10].

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of organoplatinum and -palladium compounds were carried out under an atmosphere of dry argon by use of standard procedures [11]. Solvents were dried [12], distilled under argon and degassed before use. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. of Canada and M-H-W Laboratories, Phoenix, AZ. ^{1}H, ^{2}H, ^{13}C and ^{31}P NMR spectra were acquired on Bruker AM-250 and AC-300 spectrometers, and IR spectra were obtained on Perkin–Elmer Model 283B and 1600 spectrophotometers. Mass spectra (FAB and EI) were recorded on a Kratos VG70-250S spectrometer by Mr. David C. Chang.

2.2. Materials

Reagents were procured from various commercial sources and used as received, except as noted below. The amines diethylamine, diisopropylamine and di-*sec*-butylamine were purified by distillation from NaOH. Absolute ethyl alcohol was distilled twice from $Mg(OEt)_2$. Tetracyanoethylene (TCNE) and fumaronitrile were sublimed under vacuum prior to reaction, whereas *p*-toluenesulfonyl isocyanate (TSI) was distilled from P_4O_{10}. Literature procedures were followed to synthesize the organic tosylates $PhC{\equiv}CCH_2OTs$ and $MeC{\equiv}CCH_2OTs$ (OTs = *p*-$MeC_6H_4SO_3$) [13]. The metal complexes $(PPh_3)_2Pt(C_2H_4)$ [14], $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) [15], $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C\text{-}CPh)]OTf$ (**1a**OTf, OTf = CF_3SO_3) and -OTs (**1a**OTs) [9], $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCPh)]OTs$ (**1b** OTs) [9], $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NEt_2)CHPh)]OTs$ (**6a**OTs) [9]. $[(PPh_3)_2Pd(\eta^3\text{-}CH_2C(NEt_2)CHPh)]OTs$ (**6b**OTs) [9], $Cp(CO)_2RuH$ [16], $Cp(CO)_2RuMe$ [17], Cp_2ZrH_2 [18] and $Cp_2Zr(Cl)H$ [19] were prepared by published methods. The complex $Cp_2Zr(Cl)H$ was washed with CH_2Cl_2 to remove any Cp_2ZrH_2 or Cp_2ZrCl_2 [20] immediately before use. Known $(PPh_3)Pt(\eta^3\text{-}CH_2\text{-}C(C(CO_2Me)_2)CHPh)$ (**8**) [10] was obtained in 80% yield by treatment of $NaCH(CO_2Me)_2$ in THF at −78 °C first with $(PPh_3)_2Pt(C_2H_4)$ and then with $PhC{\equiv}CCH_2OTs$, both in CH_2Cl_2, followed by warming to room temperature (r.t.), in an adaptation of the synthetic method for related complexes of platinum [9].

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

2.3.1. Reaction of *1a*OTf with $Cp(CO)_2RuH$

A solution of $Cp(CO)_2RuH$ in heptane, generated in situ from $Ru_3(CO)_{12}$ (0.026 g, 0.041 mmol) and C_5H_6, was added to a solution of **1a**OTf (0.100 g, 0.102 mmol) in 10 ml of THF at −78 °, and the mixture was allowed to warm to r.t. over 3.5 h with stirring. The solvent was removed under reduced pressure, and the solid residue was recrystallized from 11 ml of 3/8 (by volume) CH_2Cl_2–hexanes to afford $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHC(Ph)Ru(CO)_2Cp)]OTf$ (**2**OTf) as a pale yellow powder. The yield was 0.090 g (73%). IR (CH_2Cl_2): ν(CO) 2023 (s), 1966 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.17 (dd, $^3J_{HH(anti)} = 11.0$ Hz, $^3J_{HH(syn)} = 7.2$ Hz, 1H, CH), 5.10 (s, 5H, Cp), 3.47 (br m, $^2J_{HH} < 2$ Hz, $^3J_{HH(syn)} = 7.2$ Hz, 1H, *syn*-*CH*H), 2.26 (br t, $^2J_{HH} < 2$ Hz, $^3J_{HH(anti)} = 11.0$ Hz, $J_{PH} = 10.0$ Hz, $J_{PtH} = 45$ Hz, 1H, *anti*-*CH*H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 200.0 (s, $J_{PtC} = 17.2$ Hz, CO), 199.5 (s, CO), 155.0 (s, *ipso* C of allyl Ph), 134–126 (m, Ph), 122.2 (m, $J_{PC} = 3.5$ Hz, $J_{PtC} = 28.4$ Hz, CH), 90.3 (s, Cp), 60.0 (d, $J_{PC} = 30.4$ Hz, $J_{PtC} = 132$ Hz, CH_2) (CPh signal was not observed). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.6 (d, $J_{PP} = 6.4$ Hz, $J_{PtP} = 3922$ Hz), 16.4 (d, $J_{PP} = 6.4$ Hz, $J_{PtP} = 4318$ Hz). *Anal.* Found: C, 52.60; H, 3.73. Calc. for $C_{53}H_{43}F_3O_3P_2PtRuS$: C, 52.74; H, 3.59%.

2.3.2. Reaction of *1a*OTf with $Cp_2Zr(Cl)H$

A solution of **1a**OTf (0.100 g, 0.102 mmol) in 10 ml of THF at approximately −78 °C was added to a suspension of $Cp_2Zr(Cl)H$ (0.025 g, 0.099 mmol) in 10 ml of THF also at −78 °C. The reaction was allowed to warm to r.t. over 3 h with stirring and then was concentrated under reduced pressure. A $^{31}P\{^1H\}$ NMR spectrum showed one major product, identified as $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCHPh)]OTf$ (3OTf) (vide infra); however, a 'CpZr' impurity was detected by ^{1}H NMR spectroscopy. This uncharacterized species could be in part removed by filtration of the reaction mixture, addition of hexanes to the filtrate and repeated crystallization of the precipitated **3**OTf from THF–hexanes. The yield of **3**OTf varied depending on the degree of purity desired. ^{1}H NMR ($CDCl_3$): δ 8.5–6.5 (m, 35H, Ph), 5.9 (m, $^3J_{HH(anti)} = 11$, 10.5 Hz, $^3J_{HH(syn)} \geq 0$, 1H, CH), 4.9 (dd, $^3J_{HH(anti)} = 11$ Hz, $J_{PH} = 10$ Hz, 1H, *anti*-*CH*Ph), 3.4 (br m, 1H, *syn*-*CH*H), 3.3 (t, $^3J_{HH(anti)} = 10.5$ Hz, $J_{PH} = 10$ Hz, 1H, *anti*-*CH*H) (^{195}Pt satellites were indiscernible). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135–127 (m, Ph), 112.0 (t, CH), 90.9 (d, $J_{PC} = 26.4$ Hz, *C*HPh), 66.2 (d, $J_{PC} = 26.8$ Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ

18.0 (d, $J_{PP} = 10.7$ Hz, $J_{PtP} = 4050$ Hz), 14.5 (d, $J_{pp} =$ 10.7 Hz, $J_{PP} = 4222$ Hz).

*2.3.3. Reaction of **1a**OTf with $Cp_2Zr(Cl)D$*

This reaction was carried out similarly to the preceding one, but with $Cp_2Zr(Cl)D$ in place of $Cp_2Zr(Cl)H$. The ^1H NMR spectrum of the product $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CDCHPh)]OTf$ (**3**–d_1OTf) (in $CDCl_3$) was very similar to that of **3**OTf, the major difference being the virtual absence of the central CH proton signal at δ 5.9. In the ^2H NMR spectrum there was a broad signal at δ 6.

*2.3.4. Reaction of **1a**OTf with Cp_2ZrH_2*

To a suspension of Cp_2ZrH_2 (0.0113 g, 0.0509 mmol) in 5 ml of THF at −78 °C was added **1a**OTf (0.050 g, 0.051 mmol) in 10 ml of THF also at −78 °C. The mixture was allowed to warm to r.t. over 2.5 h. A single PPh_3-containing product was observed by ^{31}P NMR spectroscopy and was identified as **3**OTf.

*2.4. Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTs$ (**1a**OTs) with amines*

*2.4.1. Reaction of **1a**OTs with $(i\text{-}Pr)_2NH$*

To a stirred solution of $(PPh_3)_2Pt(C_2H_4)$ (0.150 g, 0.201 mmol) in 10 ml of CH_2Cl_2, at 0 °C was added 0.060 g (0.201 mmol} of $PhC{\equiv}CCH_2OTs$. The solution changed color from light yellow to orange and was allowed to warm to r.t. Diisopropylamine (0.100 ml, 0.718 g ml^{-1}, 0.710 mmol) was then introduced by syringe, and stirring was continued for 30 min. All volatiles were removed under reduced pressure to leave a cream-colored solid, which was washed with hexanes (3×10 ml) and dried under vacuum for several days. The yield of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(N(i\text{-}Pr)_2)CHPh)]OTs$ (**4a**OTs) was 0.215 g (97%). ^1H NMR (CD_2Cl_2): δ 7.8–6.8 (m, 39H, Ph, C_6H_4), 4.8 (br m, 1H, C*H*Ph), 3.8 (m, 2H, C*H*Me_2), 2.7 (br m, 1H, *syn*-C*H*H), 2.3(m, 1H *anti*-CH*H*), 2.3 (s, 3H, C_6H_4*Me*), 1.3–0.9 (m, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2C1_2): δ 159.3 (t, $J_{PC} = 4.5$ Hz, $J_{PtC} = 120$ Hz, N*C*CH_2), 139–126 (m, Ph, C_6H_4), 60.2 (d, $J_{PC} = 50$ Hz, $J_{PtC} = 260$ Hz, *C*HPh), 49.4 (s, NCH). 38.0 (d, $J_{PC} = 46$ Hz, $J_{PtC} = 260$ Hz, CH_2), 20.9 (s, C_6H_4*Me*), 13.8 (s, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.7 (d, $J_{PP} = 7.5$ Hz, $J_{PtP} = 3324$ Hz), 14.7 (d, $J_{PP} = 7.5$ Hz, $J_{PtP} = 2994$ Hz). FAB MS: ^{195}Pt, *m*/*z* 935 (M^+), 719 ($Pt(PPh_3)_2^+$), 456 ($PtPPh_3^+$).

*2.4.2. Reaction of **1a**OTs with $(sec\text{-}Bu)_2NH$*

This reaction was conducted similarly to the preceding one, starting with $(PPh_3)_2Pt(C_2H_4)$ (0.150 g, 0.201 mmol), $PhC{\equiv}CCH_2OTs$ (0.060 g, 0.201 mmol) and (*sec*-Bu)$_2$NH (0.100 ml, 0.753 g ml^{-1}, 0.580 mmol). The yield of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(N(sec\text{-}Bu)_2CHPh)]OTs$ (**5a**OTs), a cream-colored solid, was 0.205 g (90%). ^1H NMR (CD_2Cl_2): δ 7.8–6.8 (m, 39H, Ph, C_6H_4), 4.8 (br m, 1H, C*H*Ph), 3.4 (m, 2H, C*H*(Me)Et), 2.7 (br s, 1H, *syn*-C*H*H), 2.3 (m, 1H, *anti*-CH*H*), 2.3 (s, 3H, C_6H_4*Me*), 1.8–0.7 (m, 16H, CH_2Me, CH_2*Me*, CH*Me*). $^{13}C\{^1H\}$ NMR(CD_2Cl_2): δ 161.2 (m, N*C*CH_2), 139–126 (m, Ph, C_6H_4), 56.7 (m, *C*HPh), 51.8 (m, NCH), 38.6 (m, C*C*H_2), 21.4 (s, C_6H_4*Me*), 12.0 (s, *C*H_2Me), 10.5. 10.3 (2s, CH*Me*, CH_2*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.4 (m), 14.4 (m). FAB MS: ^{195}Pt, *m*/*z* 963 (M^+), 719 ($Pt(PPh_3)_2^+$), 456 ($PtPPh_3^+$).

*2.5. Reactions of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCPh)]OTs$ (**1b**OTs) with amines*

*2.5.1. Reaction of **1b**OTs with $(i\text{-}Pr)_2NH$*

Diisopropylamine (0.100 ml, 0.718 g ml^{-1}, 0.710 mmol) was added by syringe to a stirred solution of **1b**OTs (0.150 g, 0.164 mmol) in 10 ml of CH_2Cl_2 at r.t. The color of the solution immediately changed from light yellow to gold, and stirring was continued for 10 min. The solvent and excess amine were removed under reduced pressure to leave a yellow solid, which was washed with hexanes (2×20 ml) and dried under vacuum for several days. The yield of pale yellow $[(PPh_3)_2Pd(\eta^3\text{-}CH_2(N(i\text{-}Pr)_2)CHPh)]OTs$ (**4b**OTs) was 0.151 g (90%). ^1H NMR (CD_2Cl_2): δ 7.8–6.9 (m, 39H, Ph, C_6H_4), 5.3 (br m, 1H, *CH*Ph), 3.6 (m, 2H, *CH*Me_2), 2.8 (m, 1H, *syn*-*CH*H), 2.7 (m, 1H, *anti*-CH*H*), 2.3 (s, 3H, C_6H_4*Me*), 1.2–1.0 (m, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 152.9 (t, $J_{PC} = 5$ Hz, N*C*CH_2), 138–126 (m, Ph, C_6H_4), 73.1 (d, $J_{PC} = 44$ Hz, *C*HPh), 48.8 (d, $J_{PC} = 39.5$ Hz, C*C*H_2), 48.7 (s, NCH), 21.2 (s, C_6H_4*Me*), 13.8 (s, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.6 (d, $J_{PP} = 31$ Hz), 22.7(d, $J_{PP} = 31$ Hz). FAB MS: ^{106}Pd, *m*/*z* 846 (M^+), 630 ($Pd(PPh_3)_2^+$), 368 ($PdPPh_3^+$).

*2.5.2. Reaction of **1b**OTs with $(sec\text{-}Bu)_2NH$*

The reaction was conducted similarly to the preceding one, starting with **1b**OTs (0.150 g, 0.164 mmol) and (*sec*-Bu)$_2$NH (0.100 ml, 0.753 g ml^{-1}, 0.580 mmol). The yield of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2C(N(sec\text{-}Bu)_2CHPh)]OTs$ (**5b**OTs), a yellow solid, was 0.128 g (75%). ^1H NMR (CD_2C1_2): δ 7.9–6.9 (m, 39H, Ph, C_6H_4), 5.4 (br m, 1H, C*H*Ph), 3.3 (br m, 2H, C*H*(Me)Et), 2.7 (br m, 2H, *syn*- and *anti*-CHH), 2.3 (s, 3H, C_6H_4*Me*), 1.8–0.5 (m, 16H, CH_2Me, CH_2*Me*, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 154.1 (m, N*C*CH_2), 138–126 (m, Ph, C_6H_4), 72.5 (m, *C*HPh), 51.5 (m, NCH), 48.2 (d, $J_{PC} = 41$ Hz, C*C*H_2), 20.9 (s, C_6H_4*Me*], 11.5 (s, *C*H_2Me), 10.1, 9.9 (2s, CH*Me*, CH_2*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.8–

21.8 (m). FAB MS, ^{106}Pd, *m/z* 874 (M^+), 630 ($Pd(PPh_3)_2^+$), 368 ($PdPPh_3^+$).

2.6. Competition reactions of $[(PPh_3)_2M(\eta^3\text{-}CH_2CCPh)]OTs$ ($M = Pt$ (**1a**OTs), Pd (**1b**OTs)) with R_2NH and R'_2NH or R_2NH and $R'OH$

The reaction of **1a**OTs with a mixture of Et_2NH and $(i\text{-Pr})_2NH$ illustrates the procedure employed.

A well stirred mixture of Et_2NH (0.0690 ml, 0.707 g ml^{-1}, 0.667 mmol) and $(i\text{-Pr})_2NH$ (1.39 ml, 0.718 g ml^{-1}, 10.0 mmol) in 5 ml of CH_2Cl_2 was added to a stirred solution of **1a**OTs prepared in situ from $(PPh_3)_2Pt(C_2H_4)$ (0.0500 g, 0.0669 mmol) and PhC≡CCH_2OTs (0.0200 g, 0.0670 mmol) in 5 ml of CH_2Cl_2. The resulting solution gradually changed color from orange to light yellow, and after 15 min, all volatiles were removed under reduced pressure and the yellow solid was dried for several hours. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed the presence of both $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NEt_2)CHPh)]OTs$ (**6a**OTs) and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(N(i\text{-Pr})_2)CHPh)]OTs$ (**4a**OTs) in the mixture. The relative intensities of the signals of *CH*Ph of each **6a**OTs [9] and **4a**OTs were used to determine the ratio of the two products.

This competition reaction was also run with the Et_2NH-$(i\text{-Pr})_2NH$ molar concentration ratios of 1/5 and 1/10.

Similar procedures were employed for reactions of **1a**OTs with mixtures of $(i\text{-Pr})_2NH$ and $(sec\text{-Bu})_2NH$ (1/5 and 1/10 M concentration ratios) and of Et_2NH and EtOH (1/10, 1/20 and 1/40 M concentration ratios). The faster reacting (smaller) amine was always in tenfold excess over the metal complex. The relative intensities of the signals of C*H*Me_2 of **4a**OTs and of C*H*(Me)Et of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NEt_2)CHPh)]OTs$ (**5a**OTs) in the former reaction, and of C*H*Ph of each **4a**OTs and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OEt)CHPh)]OTs$ [21] in the latter reaction were used (available) to determine the ratios of the (possible) products.

Reactions of **1b**OTs with each Et_2NH-$(i\text{-Pr})_2NH$ (1/5, 1/8 and 1/10 M concentration ratios) and $(i\text{-Pr})_2NH$/$(sec\text{-Bu})_2NH$ (1/5 and 1/10 M concentration ratios) were conducted similarly, except that the **1b**OTs used was an isolated solid sample rather than an in situ preparation. The ^1H NMR signals used to determine the ratios of products in the mixtures corresponded to those of the analogous platinum products.

2.7. Preparation of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2CHMe)$ (7)

A solution of $(PPh_3)_2Pt(C_2H_4)$ (0.100 g, 0.134 mmol) in 5 ml of CH_2Cl_2 was added with stirring to an excess of solid $NaCH(CO_2Me)_2$ (0.153 g, 0.996 mmol), obtained from $CH_2(CO_2Me)_2$ and NaH, and the mixture was cooled to −78 °C. One equiv. of MeC≡CCH_2OTs (0.030 g) in CH_2Cl_2 (1 ml) was slowly introduced to this solution, and the contents were stirred with warming to r.t. over 4.5 h. Solvent was removed under reduced pressure, and the residue was extracted with 20 ml portions of benzene. After the extract was filtered and concentrated, addition of approximately 60 ml of hexanes induced the precipitation of a pale yellow powder, which was collected on a filter frit, washed with hexanes and dried in vacuum for several hours. The yield of **7** was 0.090 g (75%). ^1H NMR ($CDCl_3$): δ 7.5–7.0 (m, 30H, Ph), 4.0 (br m, 2H, C*H*Me, *syn-CH*H), 3.52 (s, 6H, CO_2Me), 2.40 (d, $J_{PH} = 9.5$ Hz, $J_{PtH} = 61.5$ Hz, 1H, *anti*-CH*H*), 1.05 (sept, 3H, CH*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.3 (t, $J_{PC} = 11.7$ Hz, CO_2Me), 153.8 (t, $J_{PC} = 84$ Hz, *C*CH_2), 135–125 (m, Ph), 88.1 (s, *C*CO_2Me), 61.8 (d, $J_{PC} = 37$ Hz, $J_{PtC} = 178$ Hz, *C*HMe), 50.0 (s, CO_2*Me*), 42.5 (d, $J_{PC} = 40.5$ Hz, $J_{PtC} = 171$ Hz, CH_2), 16.8 (d, $J_{PC} = 6.0$ Hz, $J_{PtC} = 48.3$ Hz, CH*Me*) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.4 (br s, J_{PP} not resolved, $J_{PtP} = 3382$ Hz), 18.4 (br s, J_{PP} not resolved, $J_{PtP} = 3003$ Hz). *Anal.* Found: C, 60.53; H, 4.99. Calc. for $C_{45}H_{42}O_4P_2Pt$: C, 59.8; H, 4.68%.

2.8. Reactions of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHR)$ ($R = Me$ (7), Ph (**8**)) with unsaturated electrophiles

2.8.1. Reaction of **8** with diethyl fumarate

A solution of **8** (0.075 g, 0.078 mmol) and diethyl fumarate (0.014 g, 0.081 mmol) in 5 ml benzene was maintained at reflux temperature. Progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 18 h, the slightly cloudy solution was filtered, the filtrate was evaporated to dryness and the residue was washed with 10 ml of Et_2O. The off-white solid $(PPh_3)_2Pt(\eta^2\text{-}trans\text{-}EtO_2CCH{=}CHCO_2Et)$ (**9**) was collected by filtration, washed with 5-ml portions of Et_2O and dried under vacuum. The yield was 0.051 g (73%). IR(C_6H_6): $\nu(CO_2)$ 1753 (s) cm^{-1}, ν(C=C of Ph) 1617 (m), 1528 (m), 1435 (m) cm^{-1}. ^1H NMR (C_6D_6); δ 8.0–6.5 (m, 30H, Ph), 4.18 (d, $J_{PH} = 3.5$ Hz, $J_{PtH} = 56$ Hz, 2H, =CH), 3.92, 3.43 (2 m, 4H, CH_2), 0.75 (t, $^3J_{HH} = 7.1$ Hz, 6H, Me). $^{13}C\{^1H\}$ NMR(C_6D_6): δ 173.0 (s, $J_{PtC} =$ 39.6 Hz, CO_2Et), 136–127 (m, Ph), 58.5 (s, CH_2), 49.0 (t, $J_{PC} = 13.5$ Hz, $J_{PtC} = 215$ Hz, =CH), 13.9 (s, Me). $^{31}P\{^1H\}$ NMR (C_6H_6): δ 25.8 (s, $J_{PtP} = 3862$ Hz). FAB MS: ^{195}Pt, *m/z* 892 (M^+), 719 ($Pt(PPh_3)_2^+$).

The washings from the filtration of **9** were combined and evaporated to dryness. The residue was extracted with 10 ml of hexanes at approximately −78 °C for 1 h, and the extract was filtered. The oil obtained after evaporation of the solvent from the filtrate contained a mixture of the organic products **10** and **11** as indicated by its ^1H NMR spectrum. Purification by passage

through a short column of silica gel with CH_2Cl_2 eluent afforded off-white needles of 1,1,4,4-tetracarbomethoxy-2,5-dimethyl-3,6-diphenyl-2,5-cyclohexadiene (**11**). The yield was 0.010 g (53%). In some instances, **11** was the only organic product observed in the ^1H NMR spectrum of the reaction solution to indicate that the isomerization of **10** to **11** was complete at that point. Selected data for **10**: ^1H NMR (C_6H_6): δ 6.23 (d, J_{HH} = 2.9 Hz, 1H of =CH_2), 5.77 (t, $J_{HH} \sim 2.6$ Hz, 1H, C*H*Ph), 4.65 (d, $J_{HH} = 2.4$ Hz, 1H of =CH_2), 4.02 (s, 3H, Me), 3.78 (s, 3H, Me). Data for **11**: ^1H NMR ($CDCl_3$): δ 7.5–7.0 (m, 10H, Ph), 4.16 (s, 3H, CO_2Me), 3.83 (s, 3H, CO_2Me), 2.41 (s, 6H, CMe). ^{13}C NMR ($CDCl_3$): δ 164.1, 161.8 (2s, *C*O_2Me), 139.5 (s, *C*Me), 130.5, 128.4, 126.7, 125.4 (s, 3d, Ph), 118.0 (s, *C*Ph), 93.1 (s, *C*CO_2Me), 57.5, 50.8 (2q, CO_2*Me*), 10.9 (q, C*Me*). EI MS: *m*/*z* 492.178 (M^+), 461 ($M^+ -$OMe), 434 ($M^+ -$OMe$-$CO), 402 ($M^+ -$2OMe$-$CO), 374 ($M^+ -$2OMe$-$2CO). 246 (M^+/2).

2.8.2. Reaction of **8** with p-toluenesulfonyl isocyanate (TSI)

A solution of **8** (0.200 g, 0.207 mmol) in 5 ml of CH_2C1_2 was treated with 3 equiv. of TSI (0.656 M solution in CH_2Cl_2) and the contents were stirred for 3 h at r.t. The solvent was removed under reduced pressure, the residue was treated with 10 ml of THF and the resulting suspension was stirred for 30 min. The white insoluble solid, $(PPh_3)_2Pt(OCNSO_2C_6H_4Me)_2$ (**12**), was collected by filtration and washed with 5-ml portions of THF. The yield was 0.042 g. IR (C_6H_6): ν(C=C) 1598 (m), 1550 (m), 1481 (m) cm^{-1}, $\nu(SO_2)$ 1020 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0–6.5 (m, 38H, Ph, C_6H_4,), 2.28 (s, 6H, C_6H_4*Me*). $^{13}C\{^1H\}$ NMR ($CDC1_3$): δ 141.0, 140.0, 134–127 (m, Ph, C_6H_4), 21.3 (s, C_6H_4*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.0 (s, $J_{PtP} = 3704$ Hz). *Anal.* Found: C, 55.70; H, 4.13; N, 2.61. Calc. for $C_{52}H_{44}N_2O_6P_2PtS_2$; C, 56.06; H, 3.98; N, 2.51%.

The last-mentioned filtrate was combined with the THF washings, and the mixture was concentrated to 5 ml and treated with 10 ml of hexanes. A slightly colored solution was separated by filtration from a yellow–orange precipitate. The filtrate was evaporated to dryness, and the residue was washed with several 10 ml portions of hexanes. Further purification could be effected by chromatography on silica gel. The yield of the [3+2] cycloaddition product of η^3-$CH_2C(C(CO_2Me)_2)CHPh$ and TSI, an off-white solid (**13**), was 0.033 g (36%). IR (C_6H_6): $\nu(CO_2)$ 1773 (s) cm^{-1}; ν(NCO) 1679 cm^{-1}; ν(C=C) 1570 (m), 1549 (m), 1436 (m) cm^{-1}; $\nu(SO_2)$ 1377 (s), 1176 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0–6.5 (m, 9H, Ph, C_6H_4), 5.83 (t, $^4J_{HH} = 2.25$ Hz, 1H, C*H*Ph), 5.60 (dd, $^2J_{HH} = 1.93$ Hz, $^4J_{HH} = 2.25$ Hz, 1H, =*CH*H), 5.33 (dd, $^2J_{HH} = 1.93$ Hz, $^4J_{HH} = 2.25$ Hz, 1H, =CH*H*), 3.79 (s, 3H, CO_2*Me*), 3.77 (s, 3H, CO_2*Me*), 2.40 (s, 3H, C_6H_4*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 165.3, 165.2 (2s, *C*O_2Me), 164.5 (s, NCO), 144.9 (s, *C*=CH_2), 136–126 (m, Ph, C_6H_4), 118.6 (s, =CH_2); 68.0 (s, *C*CO_2Me), 66.4 (s, *C*HPh), 53.4, 53.1 (2s, CO_2*Me*), 21.1 (C_6H_4*Me*). EI MS: *m*/*z* 443 (M^+), 412 ($M^+ -$OMe), 384 ($M^+ -$OMe$-$CO), 288 ($M^+ -$Ts). *Anal*. Found: C, 62.00; H, 4.94. Calc. for $C_{22}H_{21}O_7NS$: C, 61.81; H, 4.95%.

2.8.3. Reaction of 7 with tetracyanoethylene (TCNE)

To a solution of **7** (0.100 g, 0.110 mmol) in 10 ml of benzene at r.t. was added with stirring 1 equiv. of TCNE (0.014 g). The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and reached completion in 1 h. The solvent was then removed under reduced pressure, and the residue was washed with several 5 ml portions of Et_2O. The yield of **7**·TCNE (**14**) was 0.085 g (75%). ^1H NMR ($CDCl_3$): δ 8.0–6.8 (m, 30H, Ph), 4.48 (m, 1H, =C*H*Me), 3.45 (s, 3H, CO_2Me), 3.2 (br d, $^2J_{HH} = 14.8$ Hz, *CH*H), 3.05 (s, 3H, CO_2Me), 2.3 (dd, $^2J_{HH} = 14.8$ Hz, $J_{PH} = 9.3$ Hz, CH*H*). 1.02 (d, $J_{PH} = 7.4$ Hz, =CH*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.6, 170.1 (m, *C*O_2Me), 138–125 (m, Ph), 112.8, 112.1, 111.8, 111.2 (4s, CN), 63.3 (dd, $J_{PC} = 59$, 4 Hz, $J_{PtC} = 405$ Hz, =*C*HMe), 53.1 (dd, $J_{PC} = 38$, 5 Hz, J_{PtC} not resolved, =C), 51.8, 51.2 (2s, CO_2*Me*), 49.7 (d, $J_{PC} = 12$ Hz, *C*CO_2Me), 48.2, 43.6 (2s, *C*CN), 43.2 (d, $J_{PC} = 12$ Hz, $J_{PtC} = 63$ Hz, CH_2), 20.4 (d, $J_{PC} = 4.6$ Hz, $J_{PtC} = 31$ Hz, =CH*Me*). $^{31}P\{^1H\}$ NMR ($CDC1_3$): δ 20.5 (d, $J_{PP} = 18$ Hz, $J_{PtP} = 3839$ Hz), 20.2 (d, $J_{PP} = 18$ Hz, $J_{PtP} = 3560$ Hz). *Anal*. Found: C, 59.84; H, 4.92; N, 5.18. Calc. for $C_{51}H_{42}N_4O_4P_2Pt$: C, 59.36; H, 4.10; N, 5.43%.

2.8.4. Reaction of 7 with fumaronitrile

A solution of **7** (0.030 g, 0.033 mmol) and 2 equiv. of freshly sublimed fumaronitrile (0.005 g) in 0.5 ml of benzene-d_1 at r.t. was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy for 44 h. The in-situ spectra were consistent with the formation of $(PPh_3)_2Pt(\eta^2$-*trans*-NCCH=CHCN) (**15**), which crystallized from solution on slow evaporation of the solvent. ^1H NMR ($CDCl_3$): δ 8.0–7.0 (m, 30H, Ph), 2.57 (d, $J_{PH} = 5.9$ Hz, $J_{PtH} = 60$ Hz, 2H, C(CN)H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.0 (s, $J_{PtP} = 3709$ Hz).

The mother liquor was evaporated to dryness, and the residue was examined by ^1H NMR spectroscopy. No attempt was made at further purification of 1,4-dimethyl-2,5-dimethylene-3,3,6,6-tetracarbomethoxycyclohexane (**16**) owing to its small quantity. ^1H NMR ($CDCl_3$): δ 5.49 (d, $^2J_{HH} = 1.3$ Hz, 2H, =*CH*H), 4.88 (d, $^2J_{HH} = 1.3$ Hz, 2H, =CH*H*), 3.25 (s, 12H, CO_2Me), 2.27 (q, $^3J_{HH} = 7.1$ Hz, C*H*Me), 0.75 (d, $^3J_{HH} = 7.1$ Hz, 6H, CH*Me*).

2.8.5. Reaction of 7 with p-toluenesulfonyl isocyanate (TSI)

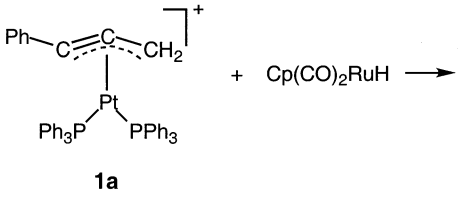
A solution of **7** (0.100 g, 0.11 mmol) in 5 ml of THF was treated with approximately 3 equiv. of TSI (0.060 g), and the contents were stirred for 12 h at r.t. The color of the solution turned bright orange during the reaction, and an abundant white precipitate formed. This precipitate, characterized spectroscopically as **12**, was filtered off, washed with 2 ml portions of THF and dried in vacuum. The yield was 0.107 g (90%). The filtrate was then treated as described in Section 2.8.2 for the analogous **13**. The yield of the [3+2] cycloaddition product (**17**) of η^3-$CH_2C(C(CO_2Me)_2)CHMe$ and TSI was 0.032 g (76%). ^{1}H NMR ($CDCl_3$): δ 7.95, 7.34 (2d, $^3J_{HH} = 8.3$ Hz, 4H, C_6H_4), 5.54 (m, 1H, =C*H*H), 5.46 (m, 1H, =CH*H*), 4.96 (q, $^3J_{HH} = 6.4$ Hz, 1H, C*H*Me), 3.75 (s, 3H, CO_2Me), 3.63 (s, 3H, CO_2Me), 2.44 (s, 3H, C_6H_4*Me*), 1.65 (d, $^3J_{HH} = 6.4$ Hz, 3H, CH*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.8, 164.7 (2s, *C*O_2Me), 164.1 (s, NCO), 154.5 (s, *C*=CH_2), 115.6 (s, =CH_2), 59.3 (s, *C*CO_2Me), 53.8, 53.6 (2s, CO_2*Me*), 29.6 (s, *C*HMe), 23.5 (s, CH*Me*), 21.6 (s, C_6H_4*Me*).

3. Results and discussion

3.1. Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (**1a**OTf) with metal hydrido complexes

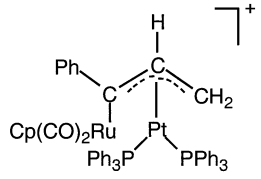
Although reactions of transition-metal η^3-allenyl/propargyls have been investigated with a number of nucleophilic reagents [1–6], those with metal hydrido complexes have not been studied. Yet metal hydrides L_xMH represent an interesting class of nucleophiles because hydride is expected to add to the central carbon atom of the η^3-allenyl/propargyl, with the L_xM fragment bonding to the terminal CR carbon. Thus, these reactions, unlike those previously reported [1–6], generate metal η^3-allyl products containing the entering heteroatom substituent in the terminal position. Furthermore, they would provide another synthetic route to bimetallic complexes.

With the aforementioned objectives in mind, we undertook a study of reaction of **1a**OTf with $Cp(CO)_2RuH$. The reaction was conducted at −78 °C with warming to r.t. and resulted in the isolation in 73% yield of a pale yellow air-stable solid, characterized by spectroscopy and elemental analysis as $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHC(Ph)Ru(CO)_2Cp)]OTf$ (**2**OTf) (Eq. (2)). This cationic product is isomeric with the complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(Ru(CO)_2Cp)CHPh)]BF_4$ (**2I**BF_4), obtained earlier by reaction of $[Cp(CO)_2Ru(\eta^2\text{-}CH_2{=}C{=}CHPh]BF_4$ with $(PPh_3)_2Pt(C_2H_4)$ [22] (Eq. (3)).

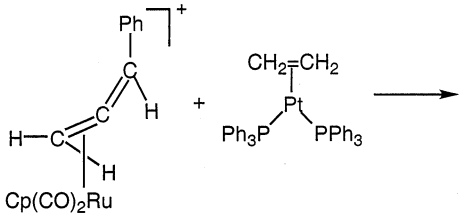


1a

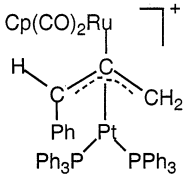
(2)



2



(3)



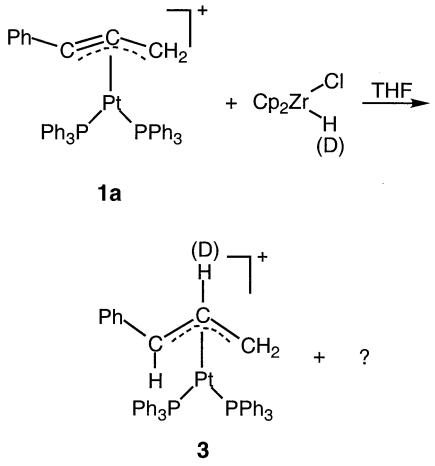
2I

The IR spectrum of **2**OTf shows two strong ν(CO) bands at 2023 and 1966 cm^{-1}. These frequencies are comparable to those of the cationic **2I**BF_4 at 2027 and 1976 cm^{-1} and the neutral $Cp(CO)_2RuCH{=}C{=}CH_2$ and $Cp(CO)_2RuCH_2C{\equiv}CPh$ at 2031 and 1984 cm^{-1} and 2014 and 1959 cm^{-1}, respectively [22]. Thus, the positive charge of **2** and **2I** is largely localized on the platinum part of the complex, consistent with the assigned structures. The ^{1}H NMR spectrum of **2**OTf displays η^3-allyl signals at δ 6.17, 3.47 and 2.26, which are attributed to CH, *syn*-C*H*H and *anti*-CH*H*, respectively. The signal at δ 2.26 occurs with readily discernible coupling to one phosphorus (10.0 Hz) and to platinum-195 (45 Hz), as expected for a η^3-allyl *anti* proton [9,10,21,23,24]. The coupling constants $^2J_{HH} < 2$ Hz, $^3J_{HH(anti)} = 11.0$ Hz and $J_{HH(syn)} = 7.2$ Hz, all consistent with the proposed structure [25], were determined with the aid of decoupling experiments. The $^{13}C\{^1H\}$ resonances of the η^3-allyl ligand are observed at δ 122.2 ($J_{PC} = 3.5$ Hz, $J_{PtC} = 28.4$ Hz) for CH and 60.0 ($J_{PC} = 30.4$ Hz; $J_{PtC} = 132$ Hz) for CH_2, again in

accord with the structural assignment. However, no signal was detected for the *C*Ph carbon, possibly owing to its presumed low intensity. The presence of the $Cp(CO)_2Ru$ moiety in **2** is reflected by the appearance of the CO resonances at δ 200.0 and 199.5 and of the Cp resonance at δ 90.3. It is noteworthy that the signal at δ 200.0 shows platinum-195 satellites, with $J_{PtC} = 17.2$ Hz. Similar, but smaller (8.8–9.3 Hz), J_{PtC} coupling was reported [22] for the CO's of **2I**BF_4. The magnitude of the J_{PtC} for **2**OTf might indicate that the $Cp(CO)_2Ru$ is positioned *anti* as a substituent on the η^3-allyl ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2**OTf is typical of those for $Pt(PPh_3)_2$ complexes containing an unsymmetrical η^3 hydrocarbyl group [9,10,21].

Since $Cp(CO)_2RuH$ was found to add to the η^3-allenyl/propargyl ligand of **1a**OTf, it was of interest to determine whether the related alkyl complex $Cp(CO)_2RuMe$ would behave similarly. However, no reaction was observed by ^{31}P NMR spectroscopy between **1a**OTf and $Cp(CO)_2RuMe$ in CH_2C1_2 at reflux temperature.

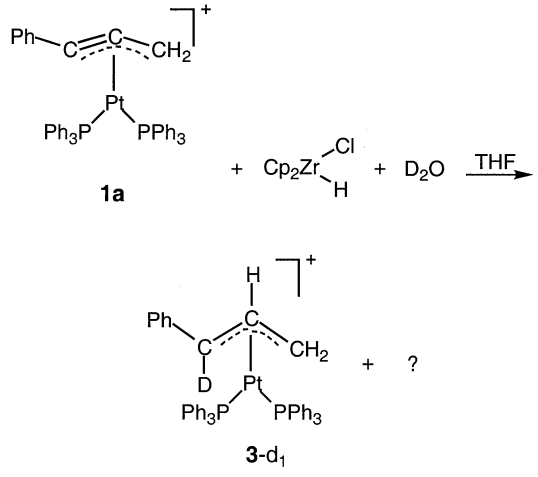
Our investigation of reactions of **1a**OTf with metal hydrides was then extended to the early transition metals represented by $Cp_2Zr(Cl)H$. Treatment of $Cp_2Zr(Cl)H$ with **1a**OTf in THF at −78 °C with warming to r.t. afforded [$(PPh_3)_2Pt(\eta^3$-CH_2CH-CHPh)]OTf (**3**OTf) as the only organometallic product that could be isolated and characterized (Eq. (4)). The fate of the Cp_2ZrCl moiety was not determined. The η^3-allyl complex **3**OTf was synthesized earlier from $Pt(PPh_3)_4$ and $PhCH{=}CHCH_2HgCl$ by Nesmeyanov and Rubezhov [26], but spectroscopic details were not disclosed. In this study, the structure of **3**OTf was inferred with the aid of NMR data. Thus, the ^1H NMR spectrum shows η^3-allyl signals at δ 5.8, 4.9, 3.4 and 3.3, which are assigned to the CH, *anti*-C*H*Ph, *syn*-C*H*H and *anti*-CH*H* protons, respectively, with the help of decoupling experiments. The coupling constants J_{HH} are given Section 2.3.2. The magnitude of $^3J_{HH}$ between CH and C*H*Ph (11 Hz) indicates an *anti* arrangement of two protons [25]. This arrangement receives further support by the absence of *W*-coupling, which would he expected for a η^3-allyl containing two *syn* hydrogens [27]. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra are also in accord with the η^3-allyl structure. The former shows signals at δ 112.0 (CH), 90.9 (*C*HPh) and 66.2 (CH_2), whereas the latter consists of two doublets al δ 18.0 ($J_{PtP} = 4050$ Hz) and 14.5 ($J_{PtP} = 4222$ Hz) with $J_{PP} = 10.7$ Hz. When the reaction in question was carried out by using $Cp_2Zr(Cl)D$ in place or $Cp_2Zr(Cl)H$, **3**–d_1OTf was obtained with deuterium exclusively at the central carbon atom (cf. Eq. (4)). Reaction between **1a**OTf and Cp_2ZrH_2, also afforded **3**OTf.



(4)

A point that remains to be addressed is the source of the C*H*Ph hydrogen in the **3**OTf synthesized by reaction of **1a**OTf with $Cp_2Zr(Cl)H$. To ascertain whether this hydrogen derives from solvent, the reaction was carried out in each of THF-d_8, benzene and benzene-d_6. It was found to proceed very slowly in benzene owing to low solubility of the reactants. However, in all cases, **3**OTf was obtained as the product, and no labeling was observed when deuterated solvents were employed.

In order to determine whether adventitious H_2O was the source of the above hydrogen, a solution of **1a**OTf in THF was treated first with 2 equiv. of D_2O and then immediately with $Cp_2Zr(Cl)H$. The η^3-allyl product isolated from the reaction mixture contained approximately 80% deuterium incorporation into the C*H*Ph position (Eq. (5)) as ascertained by ^1H NMR spectroscopy.



(5)

Furthermore, the ^2H NMR spectrum of the product showed a signal at δ 4.8. No labeling at the other positions was inferred or found by ^1H or ^2H NMR spectroscopy. Thus, it appears that the C*H*Ph hydrogen in **3**OTf originates from adventitious H_2O in the solvent. We consider it unlikely that this H_2O in very low concentration reacts with **1a**OTf to yield the oxygen-

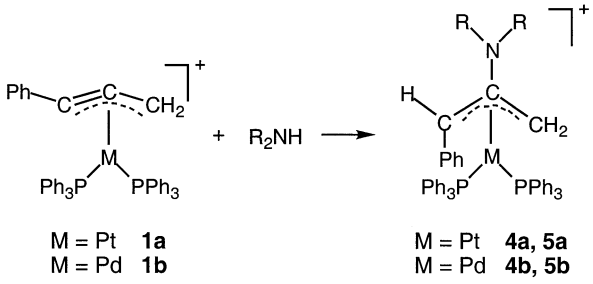
bridged binuclear [{$(PPh_3)_2Pt(\eta^3$-CH_2CCH-Ph)$\}_2O$](OTf)$_2$ [21], which is then converted by $Cp_2Zr(Cl)H$ to **3**OTf. This is because reaction of **1a**OTf with H_2O [21] was found to proceed quite slowly compared with the formation of **3**OTf.

In conclusion, we propose that $Cp_2Zr(Cl)H$ reacts with **1a**OTf to afford a platinacyclobutene intermediate, which is protonated by H_2O at platinum and then converted to **3**OTf by hydrogen transfer to =CPh. Alternatively, the initial product of the reaction might be a η^3-allyl complex, [$(PPh_3)_2Pt(\eta^3$-$CH_2CHC(Ph)$-$Zr(Cl)Cp_2)$]OTf, analogous to **2**OTf, which undergoes transformation to **3**OTf by the action of H_2O. Both of these mechanistic possibilities are depicted in Scheme 1.

3.2. Reactions of [$(PPh_3)_2M(\eta^3$-CH_2CCPh]OTs (M = Pt (**1a**OTs), Pd (**1b**OTs)) with amines

Nucleophilic addition reactions of primary and secondary amines with platinum and palladium η^3-allenyl/propargyl complexes have been the subject of several reports [7–9,28]. However, unlike the corresponding reactions of alcohols [21,24], these additions have not been investigated with respect to relative reactivity of various amines. We set out to fill this void, but first considered it necessary to augment published synthetic studies [7–9] to obtain a series of structurally related η^3-(2-aminoallyl) complexes of platinum and palladium.

Reactions of **1a**OTs and **1b**OTs (the former prepared in situ from $(PPh_3)_2Pt(C_2H_4)$ and PhC≡CCH_2OTs [9]) with an excess of the secondary amine $(i\text{-Pr})_2NH$ or $(sec\text{-Bu})_2NH$ in CH_2Cl_2 solution proceed readily at r.t. to afford the appropriate η^3-(2-aminoallyl) complexes [$(PPh_3)_2M(\eta^3$-$CH_2C(NR_2)CHPh$)]OTs (R = *i*-Pr, M = Pt (**4a**OTs), Pd (**4b**OTs); R = *sec*-Bu, M = Pt (**5a**OTs), Pd (**5b**OTs) as cream-colored (M = Pt) or yellow (M = Pd) solids in 75–97% isolated yield (Eq. (6)). The products are stable in the solid for several days; however, they decompose in solution when exposed to air and moisture. They also decompose, without melting, upon heating at 70–100 °C.



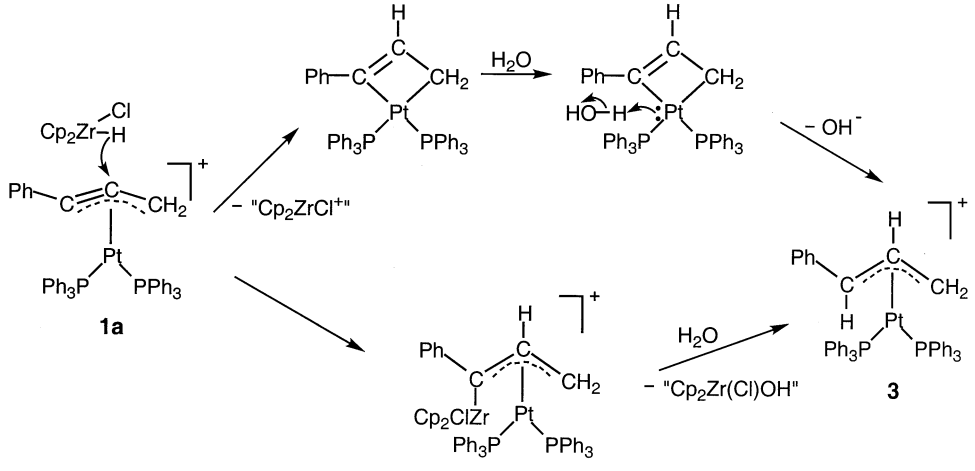
M = Pt **1a** M = Pd **1b**

M = Pt **4a, 5a** M = Pd **4b, 5b**

(6)

The new complexes were characterized by NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy and FAB MS. Each mass spectrum showed a strong peak corresponding to the parent molecular ion, as well as peaks for $M(PPh_3)_2^+$ and $MPPh_3^+$. The NMR spectra are in good agreement with those of the related η^3-(2-aminoallyl) complexes of platinum and palladium [$(PPh_3)_2M(\eta^3$-$CH_2C(NHR$ or $NR_2)CHR'$)]$^+$ (M = Pt, Pd; R = alkyl, aryl; R′ = Ph, Me, H) [7–9,28] and exhibit additional features as mentioned below.

The ^1H NMR signals of the η^3-allyl framework occur as relatively broad miltiplets at δ 4.8, 2.7 and 2.3 for the platinum complexes, and δ 5.4–5.3, 2.8–2.7 and 2.7–2.3 for the palladium complexes. By comparison with the spectra of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(NR_2)CHPh$)]$^+$ (R = Me, Et (**6a**)) [7,9] and [$(PPh_3)Pd(\eta^3$-$CH_2C(NEt_2)CHPh$)]$^+$ (**6b**), these signals are assigned to the C*H*Ph, *syn*-C*H*H and *anti*-CH*H* protons, respectively. Similar appearance of the corresponding resonances in the spectra of all of these complexes suggests that they possess the same orientation of Ph and NR_2, viz., *anti*. This stereochemistry was previously inferred for **6a**OTf with the aid of proton decoupling experiments [9].



Scheme 1.

In the $^{13}C\{^1H\}$ NMR spectra, resonances of the η^3-allyl framework are observed at δ 161.2–159.3, 60.2–56.7 and 38.6–38.0 for the platinum complexes **4a**OTs and **5a**OTs, and at δ 154.1–152.9, 73.1–72.5 and 48.8–48.2 for the palladium complexes **4b**OTs and **5b**OTs. Their assignment to the $NCCH_2$, *C*HPh and CH_2 carbon atoms, respectively, again is based on comparison with the spectra of related complexes [7–9,21,23,24,28] and on characteristic splitting patterns. Thus, the signal of $NCCH_2$ sometimes shows small phosphorus–carbon coupling involving both phosphorus atoms (triplet, $J_{PC} = \sim 5$ Hz), whereas the signals of *C*HPh and CH_2 display larger coupling, to only one phosphorus (doublet, $J_{PC} = 40–50$ Hz), and occur in conjunction with platinum-195 satellites ($J_{PtC} = 260$ Hz) for **4a**OTs and **5a**OTs.

Significantly, the η^3-(2-aminoallyls) containing (*sec*-Bu)$_2$N (i.e. **5a**OTs and **5b**OTs) show more complex signals in their NMR spectra than the η^3-(2-aminoallyls) containing (*i*-Pr)$_2$N (i.e. **4a**OTs and **4b**OTs). These differences are attributed to the fact that **5a**OTs and **5b**OTs each possess two chiral centers in the dialkylamino group, and, therefore, exist as a mixture of diastereomers. The $^{31}P\{^1H\}$ NMR spectra, especially, are conspicuously dissimilar. Whereas the spectra of **4a**OTs and **4b**OTs appear as the usual doublet-of-doublets patterns [7–9,21], with platinum-195 satellites for **4a**OTs, those of **5a**OTs and **5b**OTs present themselves as complex multiplets.

The relative reactivities of **1a**OTs and **1b**OTs toward the secondary amines Et_2NH, (*i*-Pr)$_2$NH and (*sec*-Bu)$_2$NH at r.t. were elucidated by competition experiments using mixtures of two amines as described in Section 2.6. It was determined that, toward **1a**OTs, Et_2NH is approximately 74 times more reactive than (*i*-Pr)$_2$NH (standard deviation (S.D.) = 2), and (*i*-Pr)$_2$NH is about 3.5 times more reactive than (*sec*-Bu)$_2$NH (S.D. = 0.2). The palladium complex **1b**OTs reacts 38 times faster (S.D. = 5) with Et_2NH than with (*i*-Pr)$_2$NH, and five times faster (S.D. = 0.4) with (*i*-Pr)$_2$NH than with (*sec*-Bu)$_2$NH. Thus, overall reactivity decreases in the order Et_2NH (74) > (*i*-Pr)$_2$NH (3.5) > (*sec*-Bu)$_2$NH (1) for **1a**OTs, and Et_2NH (38) > (*i*-Pr)$_2$NH (5) > (*sec*-Bu)$_2$NH (1) for **1b**OTs. The two rate profiles are very similar and indicate that steric demands of the amine are most important in determining relative reactivity. Steric properties of the amines are reflected by the values of their cone angles, with Et_2NH (125°) < (*i*-Pr$_2$)NH (137°) < (*sec*-Bu)$_2$NH (158°) [29]. In contrast, the relative basicity of the amines used in this study—$K_b = 1.4 \times 10^{-3}$ for Et_2NH, 1.6×10^{-3} for (*i*-Pr)$_2$NH and 1.8×10^{-4} for (*sec*-Bu)$_2$NH [30]—do not rationalize the observed trends.

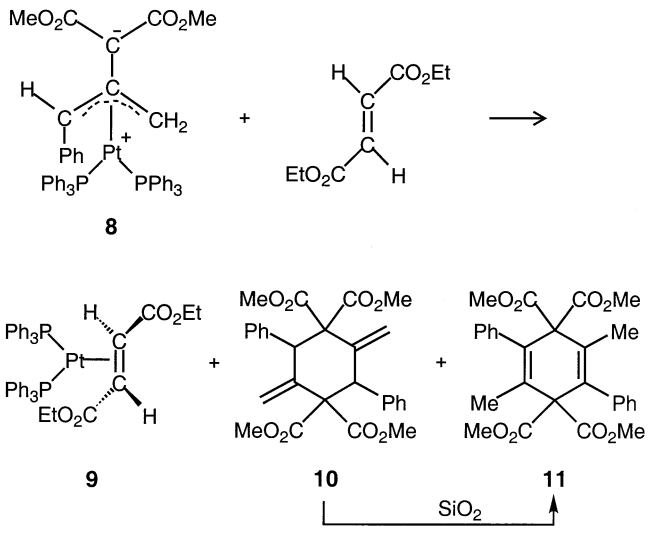
Competition reaction of **1a**OTs was also conducted with mixtures of Et_2NH and EtOH. Only the η^3-(2-aminoallyl) product **6a**OTs was detected to indicate that nucleophilic addition of Et_2NH is much faster than that of EtOH. This result may be attributed to a much greater basicity of Et_2NH compared with EtOH (e.g. $K_b = 1.4 \times 10^{-3}$ and 5.0×10^{-17}, respectively [30]). Furthermore, amines are stronger nucleophiles than alcohols [31]. Both of these factors override a comparatively small steric advantage of EtOH over Et_2NH.

3.3. Reactions of $(PPh_3)_2Pt(\eta^3$-$CH_2C(C(CO_2Me)_2)CHR)$ ($R = Me$ (**7**), Ph (**8**)) with unsaturated electrophiles

Our group previously reported the synthesis of a η^3-trimethylenemethane (η^3-TMM) complex of platinum, **8**, by reaction of **1a** with $NaCH(CO_2Me)_2$ [10]. The preparation of an analogous palladium complex, $(PPh_3)_2Pd(\eta^3$-$CH_2C(C(CO_2Me)_2)CH_2)$, was communicated by Chen and coworkers [32]. Both complexes undergo [3+2] cycloaddition reactions with unsaturated electrophiles; however, our study of such reactions of **8** was limited to TCNE. Here we report further investigations on the behavior of **8** toward unsaturated electrophiles, as well as the preparation of a related η^3-TMM complex of platinum, **7**, and its corresponding chemistry. Platinum η^3-TMM complexes were recently reviewed [33].

In an exploratory study, complex **8** in benzene solution was treated with several electron-deficient alkenes and alkynes, including diethyl fumarate, fumaronitrile, malononitrile and dimethylacetylene dicarboxylate. No reaction was observed at r.t.; however, upon allowing these solutions to remain at reflux temperature for 18 h, all of **8** was consumed. $^{31}P\{^1H\}$ NMR spectra indicated the formation of appropriate $(PPh_3)Pt(\eta^2$-alkene or -alkyne) as the only platinum-containing product [34–36]. Since all of these electophilic reagents appeared to show similar behavior toward **8**, only one of them, viz., diethyl fumarate, was selected for a detailed study.

The reaction between **8** and diethyl fumarate in benzene solution at reflux temperature afforded $(PPh_3)_2Pt(\eta^2$-*trans*-$EtO_2CCH{=}CHCO_2Et)$ (**9**) and two organic products, **10** and **11**, derived by [3+3] coupling of η^3-TMM (Eq. (7)). Complex **9** was characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and FAB MS. The ^1H NMR spectrum exhibits a characteristic resonance of coordinated alkene as a doublet of δ 4.18 ($J_{PH} = 3.5$ Hz) with platinum-195 satellites ($J_{PH} = 56$ Hz), as well as two signals of the diastereotopic ethyl CH_2 protons as multiplets at δ 3.92 and 3.43. The $^{13}C\{^1H\}$ resonances of the equivalent carboethoxy carbonyl groups and the olefinic carbons provide evidence for interaction with the metal: δ 173.0 (s, $J_{PtC} = 39.6$ Hz, CO_2Et) and 49.0 (t, $J_{PC} = 13.5$ Hz, $J_{PtC} = 215$ Hz, =CH). There is, as expected, a single $^{31}P\{^1H\}$ resonance (δ 25.8, $J_{PtP} = 3862$ Hz).



(7)

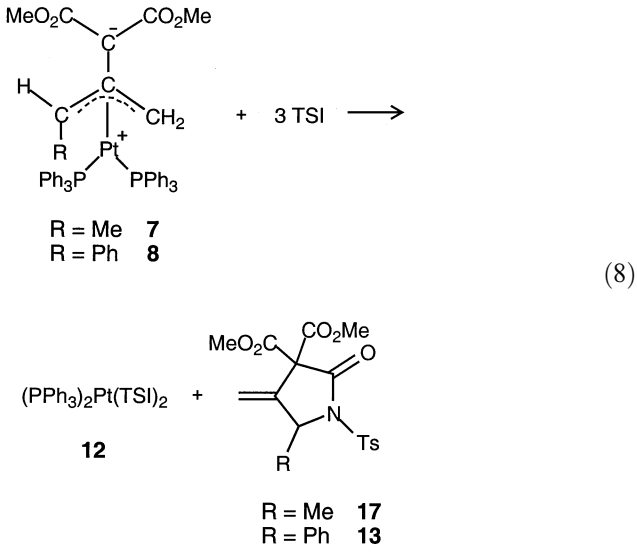
The ratio of the organic products **10/11** depends on reaction and workup conditions. Isomerization of **10** to **11** was found to occur in part during the reaction and could be promoted further by elution of the mixture through a silica gel column. Compound **10** was not isolated pure, and the isolation of pure **11** required several extraction steps to achieve complete separation from **9** (cf. Section 2.8.1).

The assigned structure of **10** is supported by the presence of two vinylic (=CH_2) ^{1}H resonances at δ 6.23 and 4.65 as doublets and an allylic (C*H*Ph) resonance at δ 5.77 as a triplet ($J_{HH} \sim 2.6$ Hz). Upon isomerization of **10** to **11**, these resonances disappear and are replaced by a singlet methyl signal (CMe) at δ 2.41. In the ^{1}H NMR spectrum of each compound, the carbomethoxy Me groups resonate as two singlets: at δ 4.02 and 3.78 for **10** and at δ 4.16 and 3.83 for **11**. The ^{13}C{^{1}H} NMR spectrum of **11** is in agreement with the proposed structure, and the EI mass spectrum confirms the dimerization of η^3-TMM by showing a parent mass peak at *m*/*z* 492.178 and an intense peak at *m*/*z* 246 that corresponds to $M^+/2$.

The importance of diethyl fumarate in the formation of **10** from **8** is underscored by the stability of **8** to thermolysis in benzene at reflux temperature in the absence of the fumarate. It is not known whether the role of diethyl fumarate is to initiate the dimerization of η^3-TMM or to prevent the retrodimerization process by irreversibly coordinating to the platinum fragment. To our knowledge, the transformation in question represents the only reported example of such a transition metal-promoted coupling reaction.

The observed lack of reactivity between the η^3-TMM ligand of **8** and electrophilic alkenes and alkynes suggested that the more polarized unsaturated species such as isocyanates might be better reagents for the desired cycloaddition. Isocyanates have been found to participate in cycloaddition reactions involving the η^3-azatrimethylenemethane ligand of $(PPh_3)_2Pt(\eta^3$-$CH_2C(NR)CHPh)$ (R = 4-MeC_6H_4, 4-$NO_2C_6H_4$) [8] and the η^3-azatrimethylenemethane and η^3-oxatrimethylenemethane ligands of platinum and palladium complexes that were generated in situ [37,38].

Initial studies conducted on solutions containing **8** and PhNCO in benzene showed that there was no detectable reaction in 10 h at reflux temperature. In contrast, when **8** was allowed to react with 3 equiv. of the more electrophilic TSI for 3 h at r.t., a platinum complex analyzing for $(PPh_3)_2Pt(OCNSO_2C_6H_4Me)_2$ (**12**) and an organic cycloadduct, **13**, were isolated (Eq. (8)).



(8)

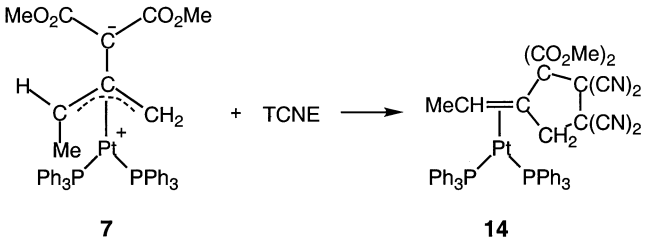
The ^{1}H NMR spectrum of **12** revealed a C_6H_4Me singlet at δ 2.28 and an aromatic multiplet at δ 8.0–6.5 in a ratio of 3/19 that corresponds to one PPh_3 for each TSI. However, a carbonyl resonance of TSI could not be definitely assigned in the ^{13}C{^{1}H} NMR spectrum. Moreover, the FAB mass spectrum showed the highest peak to occur at *m*/*z* 1087, which most likely arises from the loss of a CO by the molecular ion of **12**. Unfortunately, spectroscopic data did not allow the mode of coordination of the TSI ligands to be elucidated. Attempts to grow crystals of the complex for an X-ray diffraction study proved unsuccessful.

The organic product **13** was characterized as a [3+2] cycloadduct of η^3-TMM and TSI on the basis of elemental analysis, EI mass spectrum and IR and NMR spectroscopic data. Its NMR spectra indicate that the cyclization occurred at the $C(CO_2Me)_2$ and *C*HPh centers of η^3-TMM. Thus, the ^{1}H NMR spectrum shows the presence of an exocyclic C=CH_2, double bond (δ 5.60, dd; δ 5.33, dd; $^2J_{HH} = 1.93$ Hz, $^4J_{HH} = 2.25$ Hz) and an allylic proton (δ 5.83, t, $^4J_{HH} =$ 2.25 Hz). As expected, the two carbomethoxy groups are inequivalent and resonate as two singlets at δ 3.79 and

3.77. The $^{13}C\{^1H\}$ NMR spectrum is characterized of a five-membered lactam substrate, with three carbonyl resonances being observed: at δ 165.3 and 165.2 for the two carbomethoxy groups, and at δ 164.5 for the amide carbonyl group [39]. The presence of an exocyclic C=CH_2 bond is confirmed by the appearance of two olefinic resonances, at δ 144.9 and 118.6. The structure of **13** is similar to that proposed for the organic cycloadducts obtained from $(PPh_3)_2Pt(\eta^3$-$CH_2C(NR)CHPh)$ (R = 4-MeC_6H_4, 4-$NO_2C_6H_4$) and TSI [8].

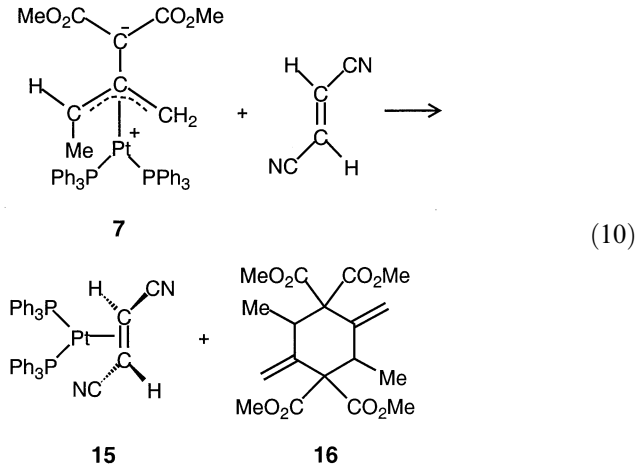
In order to test the generality of the aforementioned behavior of platinum η^3-TMM complexes toward unsaturated electrophiles we endeavored to extend this study to the methyl-substituted analog of **8**, viz., $(PPh_3)_2Pt(\eta^3$-$CH_2C(C(CO_2Me)_2)CHMe)$ (**7**). This complex was prepared in 75% yield by treatment of a mixture of $(PPh_3)_2Pt(C_2H_4)$ and $NaCH(CO_2Me)_2$ with $MeC{\equiv}CCH_2OTs$, and was characterized by elemental analysis and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Its spectroscopic properties (cf. Section 2.7) show features that are similar to those of **8** and the η^3-2-alkoxyallyl and η^3-2-aminoallyl complexes $[(PPh_3)_2Pt(\eta^3$-$CH_2C(OR)CHMe)]^+$ and $[(PPh_3)_2Pt(\eta^3$-$CH_2C(NR_2)CHMe)]^+$, respectively [9]. The proposed *anti* disposition of the $C(CO_2Me)_2$, and Me groups on the η^3-$CH_2C(C(CO_2Me)_2)CHMe$ ligand receives evidence from selective ^1H NMR decoupling experiments. Thus, irradiation at the frequency of the C*H*Me and *syn*-C*H*H protons (δ 4.0) collapses the apparent septet at δ 1.05, assigned to CH*Me*, to a doublet. The doublet splitting is attributed to J_{PH} that involves one PPh_3 phosphorus and suggests an *anti* position of the Me group. The *anti* proton of CH_2 resonates as a doublet (J_{PH} = 9.5 Hz) with platinum-195 satellites (J_{PtH} = 61.5 Hz) at δ 2.40. Furthermore, as for **8**, the two carbomethoxy methyl groups are equivalent and give rise to a sharp singlet at δ 3.52. The carbomethoxy carbonyl and methyl groups also produce one ^{13}C resonance each, at δ 170.3 (t, J_{PC} = 11.7 Hz) and 50.0 (s), respectively.

Reaction of **7** with 1 equiv. of TCNE in benzene at r.t. afforded a 1/1 adduct of the reactants, **14**, which was characterized by chemical analysis and NMR spectroscopy as a platinum(0) alkene complex, with the alkene being derived by [3+2] cycloaddition of TCNE to the η^3-TMM ligand (Eq. (9)). The ^1H NMR spectrum of **14** shows a multiplet signal at δ 4.48, assigned to the exocyclic =C*H*Me, and resonances at δ 3.2 and 2.3 with a large geminal J_{HH} (14.8 Hz), assigned to the ring CH_2. In the $^{13}C\{^1H\}$ NMR spectrum, signals are observed for all of the inequivalent carbon atoms: two for each of *C*O_2Me, CO_2*Me* and *C*$(CN)_2$, and four for CN. Olefinic carbon atoms resonate, as expected, at δ 63.3 (=*C*HMe) and 53.1 (=C), the former with a large J_{PtC} of 405 Hz. Coordination of an unsymmetrical alkene to platinum(0) is also indicated by the appearance of two $^{13}P\{^1H\}$ resonances with similar values of J_{PtP}. The aforementioned data compare well with those for the adduct derived from **8** and TCNE, which has been assigned the same type of structure [10].



(9)

The behavior of **7** toward fumaronitrile, shown in Eq. (10), is similar to that of **8** toward diethyl fumarate. After a solution of **7** and fumaronitrile in benzene had been stored for 44 h at r.t., known $(PPh_3)_2Pt(\eta^2$-*trans*-NCCH=CHCN) (**15**) [34] was crystallized from the reaction mixture and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Evaporation of the remaining solution afforded the organic cycloadduct **16**, which showed ^1H NMR signals of the exocyclic $=CH_2$ at δ 5.49 and 4.88 as doublets with $^2J_{HH}$ = 1.3 Hz and the signal of C*H*Me at δ 2.27 as a quartet with $^2J_{HH}$ = 7.1 Hz, in addition to the methyl signals of CO_2Me and CH*Me* at δ 3.25 and 0.75, respectively. Unlike **10**, which readily isomerized to **11** upon attempted chromatography on silica gel, **16** decomposed during such treatment.



(10)

The reaction of **7** with 3 equiv. of TSI at r.t. proceeds analogously to the corresponding reaction of **8** (cf. Eq. (8)). Accordingly, the products are the platinum complex **12** and the [3+2] cycloadduct of η^3-TMM and TSI, **17**. The NMR spectra of **17** compare closely with those of **13**. Especially noteworthy is the occurrence of two proton signals for each of $=CH_2$ and CO_2Me and of two ^{13}C signals for each of *C*O_2Me and CO_2*Me*, with the chemical shifts very similar to those in the spectra of **13**.

The resonances of NCO and C=CH_2, also appear in expected positions [39,40].

In summary, our studies revealed two patterns of reactivity of the η^3-TMM complexes $(PPh_3)_2Pt(\eta^3$-$CH_2C(C(CO_2Me)_2)CHR)$ (R = Me (**7**), Ph (**8**)) with unsaturated electrophiles. The weaker electrophiles diethyl fumarate and fumaronitrile afford [3+3] coupling of the η^3-TMM ligand and coordination of the electrophile (E) to platinum to give $(PPh_3)_2PtE$. Strong electrophiles/polarophiles, TCNE and TSL, give [3+2] cycloaddition of the electrophile to η^3-TMM, and this cycloadduct has been isolated either free or complexed to platinum.

Acknowledgements

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