Notes

Intermolecular Cross-coupling Between η^2-Olefin and η^1-Allyl Ligands in Cationic Platinum(II) and Palladium(II) Complexes

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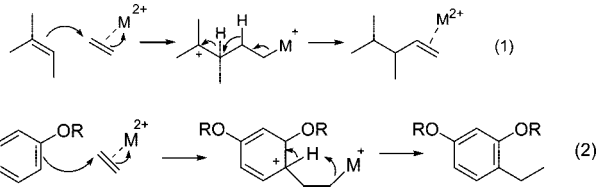
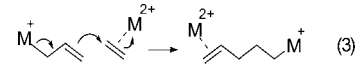
Summary: The terminal (γ) carbon atom of the allyl system in η^1-allyl platinum and palladium complexes of the tridentate pincer ligand PNP (PNP = 2,6-bis-diphenylphosphinomethyl-pyridine) attacks the coordinated olefin of dicationic platinum and palladium complexes with the same ligand, producing binuclear species in which the metal formerly π-coordinated becomes σ-bonded, and the metal formerly σ-bonded becomes π-coordinated. The reaction can be run catalytically with respect to the addition of ethylene to a η^1-allyl complex, using the dicationic ethylene complex as catalyst.

The concept that the electrophilic activation of a coordinated olefin is greatly enhanced when the metal brings a net positive charge was brought up in the chemical literature more than 20 years ago.[1] However, only in recent years has this idea been pushed further to complexes bearing a double positive charge,[2] and finally exploited to the achievement of new catalytic processes,[3] including hydroamination,[4] hydrovinylation,[5] and hydroarylation[6] reactions. In the latter two cases, the nucleophilic attack was brought about by the π-electrons of either a substituted olefin (eq 1) or an activated aromatic ring (eq 2).

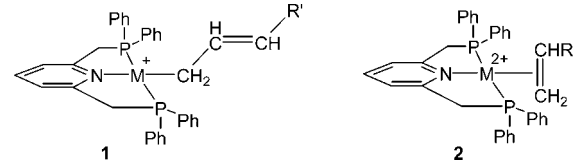


In both cases, an activation of the carbon nucleophile by electron-donating substituents was necessary to achieve an acceptable reactivity, through an adequate stabilization of the intermediate carbonium ion(s). Seeking for other π-electron nucleophilic systems capable of attacking a coordinated olefin, we considered that the double bond of a η^1-allyl complex is activated toward electrophilic attack by the presence of the metal atom in the allylic position, which would favor a concerted electron displacement as depicted in eq 3.



Indeed, the electrophilic addition to the terminus of a σ-allylmetal species is well-known,[7] and the above reaction was reported to take place between neutral $CpFe(CO)_2$(allyl) and cationic $[CpFe(CO)_2(olefin)]^+$ complexes.[8] Various allyl−olefin couplings, including the Oppolzer reaction,[9] have been shown instead to involve the alkene insertion in a σ or π-allyl metal bond,[10] and a recent theoretical investigation examined the feasibility of the analogous "ene" reaction, in which a free olefin couples to a σ-allyl moiety in a process taking place on a single metal center.[11]

In this note we report about the actual occurrence of the above allyl−olefin intermolecular coupling (eq 3), taking place between monocationic allyl complexes **1** and dicationic olefin complexes **2**, in a reaction that appears to be promising further developments.



Results and Discussion

When the stoichiometric amount of complex **1a** was added to a suspension of **2a** (both as fluoroborate salts) in dichlo-

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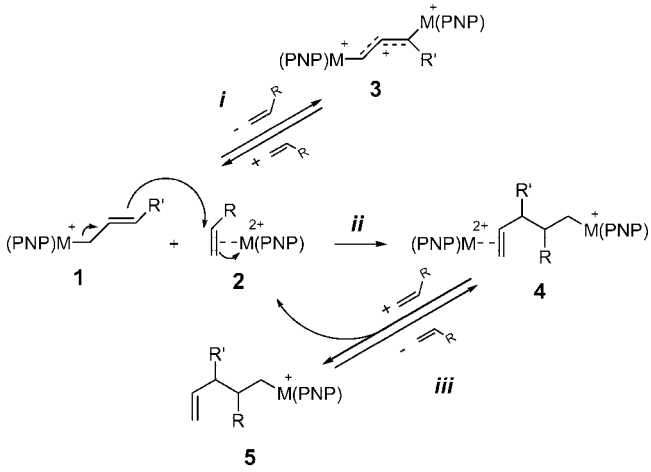
Scheme 1



(**a**) R = R' = H; (**b**) R = R' = Me; (**c**) R = H, R' = Me; (**d**) R = Me, R' = H; (**e**) R = H, R' = CH_2OMe; M = Pt, Pd

romethane, both compounds rapidly dissolved, indicating that a reaction had occurred. The ^{1}H NMR spectra of the mixture revealed that, besides the anticipated coupling reaction, displacement equilibria were taking place according to the general picture given in Scheme 1.

The initial displacement reaction (***i***) led to allyl-bridged species to whom we tentatively assign the delocalized electronic structure **3**, which accounts for the chemical equivalence of the two halves of the complex observed in the ^{13}C NMR spectrum of **3a-Pt**. The stabilization due to charge-delocalization also accounts for the observation that the ethylene displacement (***i***) is favored in the case of complex **3a**, in spite of the fact that the stability of dicationic complexes of ethylene (**2b**) is usually greater compared to complexes of higher olefins.[2] The coupling reaction (***ii***), which was particularly fast in the case of ethylene, produced the binuclear species **4**, which contains one σ-bonded and one π-bonded M(PNP) fragments. Complexes **4** were generally detected in solution by ^{1}H and ^{13}C NMR without isolation, but in the case of **4c-Pt** the complex was also obtained by ligand exchange (with elimination of ethylene) from equimolar amounts of the isolated final product **5c-Pt** and **2a-Pt**. Although the equilibrium ***i*** does actually inhibit the coupling ***ii*** (especially when R′ = H), in all the cases the overall reaction could be driven to completion by an excess of the free olefin, leading to the mononuclear species **5** and regenerating the starting alkene complex **2** via the displacement reaction ***iii***. In the case of ethylene, the overall reaction could be run catalytically with respect to the addition of free olefin to species **1**, using complex **2a** as a catalyst. In a typical experiment, ethylene was gently bubbled for 10 min at room temperature through a solution of 180 mg (0.25 mmol) of the palladium crotyl complex **1b-Pd** in 2.0 mL of dichloromethane, in the presence of 5 mol% of complex **2a-Pd**. After addition of diethyl ether and freezing to −20 °C, the coupling product **5c-Pd** was obtained essentially pure as a yellow crystalline solid (172 mg, 92% yield). The stoichiometric reaction of the propene complexes was substantially slower, a few hours being necessary to complete it at room temperature, yet still producing the corresponding complexes **5b** and **5d**. Besides their ^{1}H and ^{13}C characterization, in all the cases the structure of the reaction products **5** was confirmed by protonolysis of the M−C σ-bond with gaseous HCl in dichloromethane and identification of the resulting hydrocarbons. The coupling (***ii***) appears to be highly regioselective but not stereoselective. Indeed, in all the cases the C−C bond formation took place between the most substituted carbon atoms of the olefin and of the allyl group, but the final products **5b** were obtained as equimolar mixtures of diastereomers.

It is important to note that the η^1-allyl complexes **1** do not react with free olefins, and that the ethylene complexes **2a** do not react with η^3-allyl complexes such as [(1,5-COD)Pd(crotyl)]$^+$. The presence of a σ-allyl group on one fragment and of an electrophilically activated olefin on the other fragment are, thus, essential for the reaction to take place, and the tridentate pincer ligand PNP appears to be precisely tailored to achieve both conditions, supporting the mechanistic picture of an intermolecular "external" attack given in Scheme 1. Because this mechanism produces a nice $\sigma-\pi$ bond and net charge switching between the two metal ions involved, to get further evidence for it we reacted the palladium crotyl complex **1b-Pd** with an equimolar amount of the platinum ethylene complex **2a-Pt** in dichlorometane, and then bubbled ethylene for 10 min while mixing. The result was a 6:1 mixture of the alkyl complexes **5c-Pt** and **5c-Pd**, containing the Pt-alkyl derivative as the expected major product.[12]

In conclusion, we have demonstrated that the intermolecular "ene" coupling of a σ-allyl species with an electrophilically activated olefin is a feasible and smooth reaction, when the use of a suitable pincer ligand prevents other possible routes, such as π-allyl formation or olefin insertion reactions. Although the reaction per se is not novel, having been described almost 30 years ago in the case of cyclopentadienyl iron complexes,[8] its extension within platinum and especially palladium chemistry might prelude to interesting developments.

Experimental Section

General Procedures. CH_2Cl_2, CD_2Cl_2, CD_3NO_2, and $MeNO_2$ (free from nitriles) were dried with 4 Å molecular sieves. The NMR spectra were recorded on Varian VXR 200, Varian Gemini 300, and Brucker WH 400 instruments. The ^{1}H NMR shifts were referenced to the resonance of the residual protons of the solvents, the ^{13}C NMR shifts to the solvent resonance (δ = 53.8, CD_2Cl_2; δ = 62.8, CD_3NO_2). Abbreviations used in NMR data: s, singlet; d, doublet; t, triplet; ps. t, pseudo triplet; m, multiplet; br, broad.

Starting Materials. The palladium allyl complexes **1-Pd**[13] and the olefin complexes **2-Pd**[2a] and **2-Pt**[2b] were prepared according to the procedures described in the literature. The complex $[Pd(CH_2CHCHCH_2OMe)Cl]_2$, precursor to the methoxymethylene substituted allyl **1e-Pd**, was prepared as described.[14] The platinum complexes **1a-Pt** and **1b-Pt** (see below for NMR data) were obtained by addition of PNP to a dichloromethane solution of the corresponding bis(pyridine)[(η^3-allyl)platinum] salts, using the same procedure described for phenanthroline η^3-allyl complexes.[15]

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(12) The partial scrambling giving **5c-Pd** as a minor unexpected product can be explained by some olefin exchange taking place during the reaction time. This would produce small amounts of the Pd−ethylene complex **2a-Pd** whose reaction with **1b-Pd** gives the minor product.

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[(PNP)PtCH$_2$CH=CH$_2$](BF$_4$) (1a-Pt). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.63 (app quartet, 2 H, PtCH$_2$, J_{Pt} = 105 Hz), 4.20 (m, 2 H, =CH$_2$), 4.40 (ps t, 4 H, PCH$_2$), 5.55 (m, 1 H, =CH), 7.40−7.80 (m, 22 H, PPh, py), 8.00 (t, 1 H, py). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 5.1 ($^1J_{Pt}$ = 581 Hz, PtCH$_2$), 46.1 (ps t, ^1J_P = 34 Hz, PCH$_2$), 109.4 ($^3J_{Pt}$= 58 Hz, =CH$_2$), 123.3 (py-3,5), 127.3 (ps t, ^1J_P = 56 Hz, PPh$_j$), 129.8 (PPh$_m$), 132.6 (PPh$_p$), 133.6 (PPh$_o$), 140.4 (py-4), 143.9 ($^2J_{Pt}$ = 60 Hz, =CH), 159.6 (ps t, $^2J_{Pt}$ = 37 Hz, py-2,6).

[(PNP)PtCH$_2$CH=CHMe](BF$_4$) (1b-Pt). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.18 (d, 3 H, Me, J_{Pt} = 25 Hz), 2.57 (app quartet, 2 H, PtCH$_2$, J_{Pt} = 104 Hz), 4.40 (ps t, 4 H, PCH$_2$), 4.60 (m, 1 H, =C*H*Me), 5.15 (m, 1 H, =C*H*CH$_2$Pt), 7.50−7.90 (m, 22 H, PPh, py), 8.00 (t, 1 H, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 3.6 ($^1J_{Pt}$ = 578 Hz, PtCH$_2$), 17.7 (Me), 46.1 (ps t, ^1J_P = 33 Hz, PCH$_2$), 120.4 ($^3J_{Pt}$ = 58 Hz, =*C*HMe), 123.3 (py-3,5), 127.5 (ps t, ^1J_P = 56 Hz, PPh$_j$), 129.8 (PPh$_m$), 132.6 (PPh$_p$), 133.7 (PPh$_o$), 136.8 ($^2J_{Pt}$ = 64 Hz, =*C*HCH$_2$), 140.4 (py-4), 159.6 (ps t, $^2J_{Pt}$ = 35 Hz, py-2,6).

NMR Identification of the Allyl-bridged Complexes 3a. Species **3a** were not isolated, but were identified by their ^{1}H and ^{13}C NMR spectra. Although a full characterization of their suggested structure would be interesting, it is outside the scope of the present paper. To prepare an NMR sample containing **3a** as the largely dominant species (among those depicted in Scheme 1), 30 mg of **2a** were suspended in 2 mL of dichloromethane, and an equimolar amount of **1a**, dissolved in 1 mL of dichloromethane, was added to the mixture at room temperature. To remove any displaced ethylene, nitrogen was immediately bubbled through the solution until the volume was approximately reduced to 1 mL. The solution was finally evaporated to dryness, and the crude residue analyzed by ^{1}H and ^{13}C NMR. **3a-Pt**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.60 (d app q, 2 H, H$_{anti}$, J_{Pt} = 73 Hz), 3.00 (m, 2 H, H$_{syn}$, J_{Pt} = 102 Hz), 4.40 (app q, 8 H, PCH$_2$), 6.26 (m, 1 H, CH), 7.4−8.0 (m, 46 H, PPh, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 33.4 (CH$_2$, J_{Pt} = 340 Hz), 45.6 (ps t, ^1J_P = 33 Hz, PCH$_2$), 123.6 (py-3,5), 124.2 (ps t, ^1J_P = 58 Hz, PPh$_j$), 130.5 (PPh$_m$), 133.0 (PPh$_p$, PPh$_o$), 142.3 (py-4), 160.3 (py-2,6). **3a-Pd**. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.80 (d app t, 2 H, H$_{anti}$), 3.02 (m, 2 H, H$_{syn}$), 4.40 (ps t, 8 H, PCH$_2$), 7.10 (m, 1 H, CH), 7.3−7.9 (m, 46 H, PPh, py).

Binuclear Complex [(PNP)PtCH$_2$CH$_2$CH(Me)CH=CH$_2${Pt-(PNP)}](BF$_4$)$_3$ (4c-Pt). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.00 (m, 1 H, CH), 0.46 (d, 3 H, Me), 0.56 (m, 2 H, PtCH$_2$C*H*$_2$), 1.00 (m, 2 H, PtCH$_2$, J_{Pt} = 80 Hz), 3.98 (d ps t, 1 H, =CH*H*), 4.16 (d, 1 H, =C*H*H J_{Pt} = 70 Hz), 4.36 (ps t, 4 H, PCH$_2$), 4.56 (d ps t, 2 H, PC*H$_a$*H$_b$), 4.80 (m, 1 H, =CH), 5.10 (br, 2 H, PCH$_a$*H$_b$*), 7.30−8.10 (m, 46 H, PPh, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ −4.4 ($^1J_{Pt}$ = 635 Hz, PtCH$_2$), 17.8 (Me), 42.2 ($^3J_{Pt}$ = 35 Hz, CH), 43.2 (CH$_2$), 43.4 (ps t, ^1J_P = 33 Hz, PCH$_2$), 45.5 (ps t, ^1J_P = 33 Hz, PCH$_2$), 72.8 ($^1J_{Pt}$ = 126 Hz, =CH$_2$), 112.4 ($^1J_{Pt}$ = 123 Hz, =CH), 122.9 (py-3,5), 124.0 (py-3,5), 126.6 (ps t, ^1J_P = 55 Hz, PPh$_j$), 126.9 (ps t, ^1J_P = 55 Hz, PPh$_j$), 129.4 (PPh$_m$), 130.5 (PPh$_m$), 132−135 (PPh$_{o,p}$), 139.9 (py-4), 144.0 (py-4), 159.2 (py-2,6), 161.2 (py-2,6).

General Procedure for the Catalytic Synthesis of Complexes 5. A 150−200 mg portion of the appropriate allyl complex **1** was dissolved in 2−3 mL of dichloromethane, and 10−15 mg (ca. 5 mol %) of the ethylene complex **2a** was added at room temperature. In the case of palladium complexes, ethylene was slowly bubbled through the solution for 10−15 min, and then diethyl ether (3−5 mL) was added to the solution under ethylene atmosphere, and the solution kept at −20 °C for 1−2 h. The obtained product was essentially pure as a yellow crystalline solid. In the case of platinum complexes, the solution was stirred for 24 h at room temperature under a 2 bar pressure of ethylene and then processed as above.

[(PNP)Pd−CH$_2$CH$_2$CH$_2$CH=CH$_2$](BF$_4$) (5a-Pd). Yield 90%. Anal. Calcd for $C_{36}H_{36}BF_4NP_2Pd$: C, 58.60; H, 4.92; N, 1.90. Found: C, 58.83; H, 5.02; N, 1.82. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.35 (m, 2 H, βCH$_2$), 1.72 (app q, 2 H, γCH$_2$), 1.98 (m, 2 H, PdCH$_2$), 4.40 (ps t, 4 H, PCH$_2$), 4.66 (m, 2 H, =CH$_2$), 5.40 (m, 1 H, =CH), 7.40−7.70 (m, 22 H, PPh, py), 7.88 (t, 1 H, py). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 17.0 (PdCH$_2$), 33.2 (βCH$_2$), 37.7 (γCH$_2$), 45.0 (ps t, ^1J_P = 30 Hz, PCH$_2$), 114.3 (=CH$_2$), 123.4 (py-3,5), 128.8 (ps t, ^1J_P = 44 Hz, PPh$_j$), 129.9 (PPh$_m$), 132.3 (PPh$_p$), 133.3 (PPh$_o$), 138.6 (=CH), 140.9 (py-4), 158.4 (py-2,6).

[(PNP)PdCH$_2$CH$_2$CH(Me)CH=CH$_2$](BF$_4$) (5c-Pd). Yield 92%. Anal. Calcd for $C_{37}H_{38}BF_4NP_2Pd$: C, 59.11; H, 5.09; N, 1.86. Found: C, 58.90; H, 5.20; N, 1.80. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.60 (d, 3 H, Me), 1.25 (m, 2 H, CH$_2$), 1.70 (hept, 1 H, CH), 1.92 (m, 2 H, PdCH$_2$), 4.40 (ps t, 4 H, PCH$_2$), 4.65 (d, 2 H, =CH$_2$), 5.30 (m, 1 H, =CH), 7.40−7.70 (m, 22 H, PPh, py), 7.90 (t, 1 H, py). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 14.7 (PdCH$_2$), 19.4 (Me), 39.9 (CH$_2$), 41.3 (CH), 44.9 (ps t, ^1J_P = 26 Hz, PCH$_2$), 112.4 (=CH$_2$), 123.4 (py-3,5), 128.8 (ps t, ^1J_P = 44 Hz, PPh$_j$), 129.9 (PPh$_m$), 132.3 (PPh$_p$), 133.3 (PPh$_o$), 140.9 (py-4), 144.6 (=CH), 158.5 (py-2,6).

[(PNP)Pd−CH$_2$CH$_2$CH(CH$_2$OMe)CH=CH$_2$](BF$_4$) (5e-Pd). Yield 89%. Anal. Calcd for $C_{38}H_{40}BF_4NOP_2Pd$: C, 58.37; H, 5.16; N, 1.79. Found: C, 58.12; H, 5.25; N, 1.68. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.25 (m, 1 H, βC*H*H), 1.47 (m, 1 H, βCH*H*), 1.90 (m, 2 H, CH and PdC*H*H), 2.00 (m, 1 H, PdCH*H*), 2.92 (m, 2 H, C*H*$_2$OMe), 3.07 (s, 3 H, OMe), 4.40 (ps t, 4 H, PCH$_2$), 4.72 (d, 1 H, =CH*H*), 4.78 (d, 1 H, =C*H*H), 5.22 (ddd, 1 H, =CH), 7.45−7.75 (m, 22 H, PPh, py), 7.90 (t, 1 H, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.1 (PdCH$_2$), 34.7 (CH$_2$), 44.9 (ps t, ^1J_P = 26 Hz, PCH$_2$), 47.4 (CH), 58.7 (Me), 75.7 (CH$_2$O), 115.2 (=CH$_2$), 123.4 (py-3,5), 128.8 (ps t, ^1J_P = 44 Hz, PPh$_j$), 130.0 (PPh$_m$), 132.1 (PPh$_p$), 133.4 (PPh$_o$), 141.0 (py-4), 142.4 (=CH), 158.5 (py-2,6).

[(PNP)PtCH$_2$CH$_2$CH$_2$CH=CH$_2$](BF$_4$) (5a-Pt). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.30 (m, 2 H, βCH$_2$), 1.65 (app q, 2 H, γCH$_2$), 1.84 (m, 2 H, PtCH$_2$, J_{Pt} = 69 Hz), 4.40 (ps t, 4 H, PCH$_2$), 4.64 (m, 2 H, −CH$_2$), 5.33 (m, 1 H, −CH), 7.40−7.90 (m, 23 H, PPh, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 0.9 ($^1J_{Pt}$ = 632 Hz, PtCH$_2$), 34.3 (βCH$_2$), 38.5 ($^3J_{Pt}$ = 84 Hz, γCH$_2$), 46.2 (ps t, ^1J_P = 33 Hz, PCH$_2$), 113.9 (=CH$_2$), 123.4 (py-3,5), 128.0 (ps t, ^1J_P = 54 Hz, PPh$_j$), 130.0 (PPh$_m$), 132.5 (PPh$_p$), 133.5 (PPh$_o$), 139.1 (=CH), 140.3 (py-4), 159.6 (py-2,6).

[(PNP)PtCH$_2$CH$_2$CH(Me)−CH=CH$_2$](BF$_4$) (5c-Pt). Yield 84%. Anal. Calcd for $C_{37}H_{38}BF_4NP_2Pt$: C, 52.87; H, 4.56; N, 1.67. Found: C, 52.58; H, 4.77; N, 1.49. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.54 (d, 3 H, Me), 1.10 (m, 2 H, CH$_2$), 1.61 (hept, 1 H, CH), 1.74 (m, 2 H, PtCH$_2$, J_{Pt} = 80 Hz), 4.41 (ps t, 4 H, PCH$_2$), 4.60 (m, 2 H, =CH$_2$), 5.22 (ddd, 1 H, =CH), 7.40−7.90 (m, 22 H, PPh, py), 7.96 (t, 1 H, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ −1.9 ($^1J_{Pt}$ = 626 Hz, PtCH$_2$), 18.8 (Me), 40.9 (CH$_2$), 41.3 (CH), 45.6 (ps t, ^1J_P = 33 Hz, PCH$_2$), 111.5 (=CH$_2$), 122.9 (py-3,5), 126.3 (ps t, ^1J_P = 57 Hz, PPh$_j$), 129.4 (PPh$_m$), 132.1 (PPh$_p$), 133.1 (PPh$_o$), 139.8 (py-4), 144.4 (=CH), 159.0 (py-2,6).

Reactions of the Propene Complex 2b-Pt. These were considerably slower than the reactions of the corresponding ethylene complex and were not performed catalytically. A sample of 50 mg of **2b-Pt** was suspended in 2 mL of dichloromethane, and an equimolar amount of the appropriate allyl complex (**1a-Pt** or **1b-Pt**) was added. The solution was saturated with propene at room temperature, and the mixture was kept stirring for 24 h. The resulting solution was treated with 100 mL of acetonitrile (to remove any coordinated double bond) and evaporated to dryness. The crude residue, composed essentially by the acetonitrile complex [(PNP)Pt(MeCN)](BF$_4$)$_2$[2b] and by the Pt-alkyl complex (**5d-Pt** or **5b-Pt**) was analyzed by ^{1}H and ^{13}C NMR, without separation of the components.

[(PNP)PtCH$_2$CH(Me)CH(Me)−CH=CH$_2$](BF$_4$) (5b-Pt). (two diastereomers A and B in equal abundances). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.41 (d, 6 H, γMe$_{A,B}$), 0.52 (d, 3H, δMe$_A$), 0.55 (d, 3H, δMe$_B$), 1.40 (m, 2 H, βCH$_{A,B}$), 1.68 (m, 2H, PtCH$_{A,B}$, J_{Pt} = 82 Hz), 1.70 (m, 2 H, γCH$_{A,B}$), 2.30 (m, 2H, PtCH$_{A,B}$, J_{Pt} = 82

Hz), 4.35−4.60 (m, 8 H, PCH_2), 4.64 (d, 2 H, $=CH\mathit{H}_{A,B}$), 4.69 (d, 1 H, $=C\mathit{H}H_A$), 4.72 (d, 1 H, $=C\mathit{H}H_B$), 5.26 (ddd, 1H, $=CH_A$), 5.32 (ddd, 1H, $=CH_B$), 7.4−8.0 (m, 46 H, PPh, py).

[(PNP)PtCH$_2$CH(Me)CH$_2$−CH=CH$_2$](BF$_4$) (5d-Pt). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.52 (d, 3 H, Me), 1.40 (m, 2 H, βCH and γCH*H*), 1.80 (m, 2 H, PtCH*H* and γC*H*H), 2.12 (m, 1 H, PtC*H*H, J_{Pt} = 78 Hz), 4.5 (m, 4 H, PCH_2), 4.66 (d, 1 H, $=CH\mathit{H}$), 4.73 (d, 1 H, $=C\mathit{H}H$), 5.25 (m, 1 H, =CH), 7.40−8.10 (m, 23 H, PPh, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 12.6 ($^1J_{Pt}$ = 650 Hz, $PtCH_2$), 25.4 ($^3J_{Pt}$ = 40 Hz, Me), 41.7 (CH), 47.1 (γCH_2), 48.0 (ps t, ^1J_P = 33 Hz, PCH_2), 115.2 ($=CH_2$), 124.8 (py-3,5), 129.6 (ps t, ^1J_P = 50 Hz, PPh_j), 131.4 (PPh_m), 134.1 (PPh_p), 135.1 (PPh_o), 139.8 (=CH), 141.8 (py-4), 161.1 (py-2,6).

Protonolysis of Complexes 5. A sample of 30−50 mg of the complex (or crude mixture in the case of complexes **5b** and **5d**) was dissolved in 0.6 mL of CD_2Cl_2, and gaseous HCl was bubbled through the solution for 1 min. After 10 min the solution was filtered through a short column of silica gel (for flash chromatography) in a Pasteur pipet, eluting with an additional 0.6 mL of CD_2Cl_2. The resulting filtrate, containing the hydrocarbon(s) produced by the M−C σ-bond cleavage (together with trace amounts of the complex [(PNP)MCl](BF$_4$)) was analyzed by ^{1}H NMR, and the identity of the hydrocarbon was confirmed by comparison with published spectra. Interestingly, the sample resulting from the protonolysis of the crude mixture **5b-Pt** contained, besides the expected hydrocarbon 3,4-dimethyl-1-hexene, a minor amount (ca. 7%) of 4-methyl-1-pentene. This minor product can be explained by the formation and further reaction of a small amount of the allyl complex **1a-Pt** in the reaction mixture of **1b-Pt** with **2b-Pt**, arising from deprotonation of the propene complex **2b-Pt**.

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