行政院國家科學委員會專題研究計畫成果報告

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一、中文摘要

炔丙基及丙二烯基有機金屬錯合物與烯胺的反應形成　咯衍生物。

關鍵詞：炔丙基，丙二烯基，烯胺

Abstract

The reactions of enamines (ROC)HC=CMe(NH^{i}Pr) with η^3-allenyl/propargyl complexes $[M(PPh_3)_2(\eta^3\text{-}C_3H_3)]^+$ (M = Pd, Pt) result in the formation of the pyrrole derivatives. Such reactions involve the intermediates of central-carbon-substituted η^3-allyl complexes $\{M(PPh_3)_2(\eta^3\text{-}CH_2C[C(COR)=CMe(NH^iPr)]CH_2)\}^+$ which are formed by hydroalkenylation to C_3H_3 moiety.

Keywords: η3-allenyl/propargyl complexes, enamine.

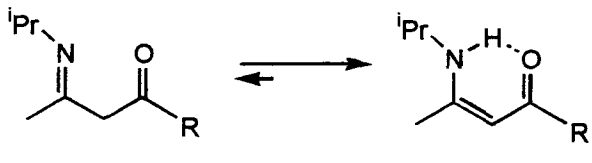
二、緣由與目的

The addition of an olefinic C–H bond across an unsaturated carbon-carbon bond is highly interesting from the viewpoint of synthetic methodology [1]. The involvement of transition metal complexes in such processes is often crucial, particularly in the aspect of developing new ways for C–C bond formation [2]. We and other groups have discovered that cationic η^3-allenyl/propargyl complexes generally behave as good carbon electrophiles and are subjected to the addition with a wide variety of nucleophiles containing O, S, Se, N, P, or C donor [3-7]. Meanwhile, such complexes exhibit keen chemical selectivity. For instance, tertiary amine such as Et_3N can be added to $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)]^+$ (**3**) via C–N bond formation to give a platinacyclobutene adduct [8]. In contrast, **3** activates a phenyl C–H bond in NMe_2Ph to succeed arylation, yielding an arylallyl complex [9].

We have chosen to use enamines that are known to contain both active N–H as well as C–H bonds to react with η^3-allenyl/propargyl complexes. Our studies lead to the discovery of the first examples of hydroalkenylation to metal complexes of allenyl/propargyl. The insertion of $\eta^3\text{-}C_3H_3$ to an enamine C–H bond affords a skeleton of "diene" which allows to incorporate with an amino functionality to transform into the pyrrole derivatives.

三、報告內容

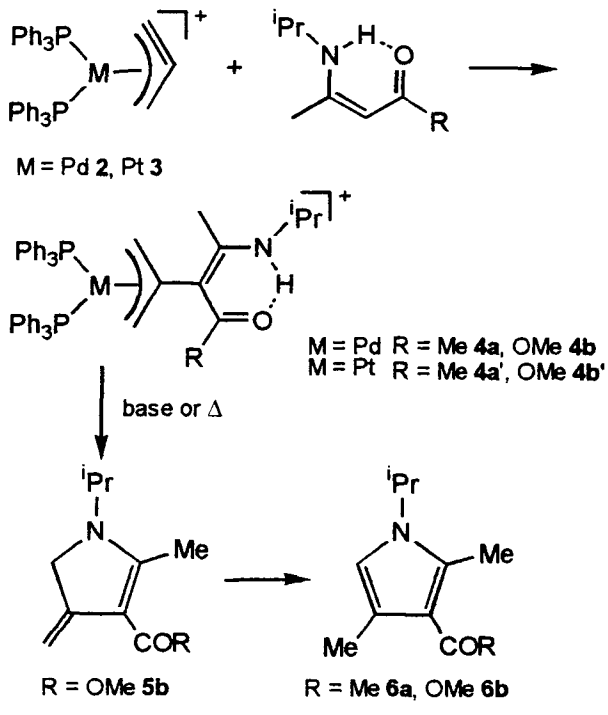
The enamines Me(NH^{i}Pr)C=CHR [R = COMe (**1a**), CO_2Me (**1b**)] have been prepared respectively by the reactions of α,γ-diketone or ketoester methane with $^iPrNH_2$ [10]. The NMR data of **1a** and **1b** indicate that tautomerization of eq. 1 overwhelmingly inclines to the enamine form which is presumably stabilized by hydrogen bonding between N–H and the keto group.



R = Me **1a**, OMe **1b**

Previous studies have shown that amines and amino derivatives with active hydrogen are prone to have regioselective hydroamination to $[M(PPh_3)_2(\eta^3\text{-}C_3H_3)]^+$ [M = Pd (**2**), Pt (**3**)], yielding azatrimethylenemethane (N-TMM) complexes and their derivatives [11]. However, heating the mixture of **2** and **1b** at 50 ℃ was found to generate the pyrrole derivatives. Deleberate investigation shows that reactions of equimolar amounts of **2** and enamine at 25 ℃ undergo unprecedented hydroalkenylation. The regioselective C–C coupling takes place between the central carbon of the C_3H_3 and the β-olefinic carbon of the enamine, and results in the enamine-allyl complexes in the formula of $Pd(PPh_3)_2\{\eta^3\text{-}CH_2C[C(COR)CMe(NH^iPr)]\text{-}CH_2\}^+$ [R = Me (**4a**), OMe (**4b**)] with the yields over 75%. Complexes **4a** and **4b** were mainly characterized by NMR techniques as well as elemental analysis. Either heating the reaction solutions of complexes **4a** and **4b** to 50 ℃, or treating them with base, the products of pyrrole derivatives **6a** and **6b** could be obtained, respectively (Scheme 1).

Scheme 1



The analogous reactions of $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**3**) with **1a** or **1b** produced $\{Pt(PPh_3)_2(\eta^3\text{-}CH_2C[C(COR)=CMe(NH^iPr)]\text{-}CH_2)\}(BF_4)$ [R = Me (**4a'**), OMe (**4b'**)] also in very good yields. The enamne-allyl platinum complexes could be formed alternatively from the reactions of *trans*-$Pt(Br)(PPh_3)_2(\eta^3\text{-}CHCCH_2)$ and enamine at 25 ℃, however, with longer reaction time. The single-crystal X-ray crystallography provides the authentic molecular structure for **4b'**. Figure 1 shows its ORTEP drawing. The length of C2-C4 is 1.46(2) Å, a typical Csp^2–Csp^2 single bond. The dihedral angle between the C1-C2-C3 and C1-Pt-C2 planes is 68(1)°, and ∠C1–C2–C3 is 113(1)°, which are consistent with the η^3-allyl characteristic and somewhat approach that of the η^3-trimethylenemethane species [7, 12]. It indicates that there is significant electronic delocalization in the planar N-C5-C4-C10-O1 moiety of enamine. The distance between N and O1 atoms is 2.52 Å that is suitable for hydrogen bonding in the vicinity. However, the generated amino hydrogen points out of the enamine plane with ∠O1–H–N = 116(7)° [13].

Ring closure in **4a'** and **4b'** could be accomplished by heating or treating with base as well, except that cyclization in **4b'** first generates a dihydropyrrole derivative **5b**. Upon chromatographing on a silica gel column, **5b** would isomerize to the stable pyrrole product **6b**. Such a reaction is mechanistically comparable to the furan formation from an enolate-allyl complex [14].

3. Conclusion

The regioselective addition of enamine to the η^3-allenyl/propargyl complexes demonstrate a new type of "alkene-alkyne" coupling which affords new enamine-allyl complexes and leads to the formation of pyrrole derivatives.

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4. Experimental Section

4.1. General

Commercially available reagents were purchased and used without purification unless necessary. Solvents were dried with use of standard procedures. All reactions and other manipulation were carried out under a nitrogen atmosphere, using standard Schlenk techniques. The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were run on either a Bruker AC-200 or ACE-300 spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency at 81.015 or 121.49 MHz was employed, and the chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in $CDCl_3$. Values upfield of the standard are defined as negative. The corresponding frequencies for ^{13}C NMR spectra were at 75.47 MHz, respectively. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin Elmer 2400 CHN analyzer.

4.2. Synthesis and Characterization

{Pd(PPh$_3$)$_2$(η^3-CH$_2$C[C(COMe)=CMe(NH^{i}Pr)]CH$_2$)}(BF$_4$) (4a). The reaction of **2** (300 mg, 0.39 mmol) and (MeOC)HC=CMe(NH^{i}Pr) (**1a**) (55 μL, 0.039 mmol) was carried out in 20 mL predried CH_2Cl_2 at -30 ℃. After stirring for 90 min, the solution was concentrated to 2 mL. Adding 20 mL of dried Et_2O gave yellow solid product. Recrystallization resulted in **4a** in 76% isolated yield (260 mg). ^{31}P NMR ($CDCl_3$, 300 MHz) δ 23.8; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21, 1.24 (3H, 3H, s, s, C$\underline{H}_3$), 2.00 (6H, d, J_{HH} = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 3.50 (2H, m, br, H_{anti}), 3.69 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 4.12 (2H, br, H_{syn}), 7.02-7.73 (30H, m, phenyl H), 12.6 (1H, d, J_{HH} = 2.2 Hz, N$\underline{H}$); ^{13}C NMR (CD$_3$CN, 300 MHz) δ 18.4, 23.7 (C$\underline{H}_3$), 30.5 (C$\underline{H}_2$), 46.2 (CO$\underline{C}$H$_3$), 80.1 (t with virtual coupling, J_{CP} = 15.4 Hz, C_t), 104.2 (C_γ), 129-134 (phosphino phenyl C), 146.1 (C_c), 165.0 (N$\underline{C}$=C), 193.7 ($\underline{C}$OMe). MS (FAB, m/z): 810 (M^+-BF_4). Anal. Calcd for $PdC_{47}H_{48}NOP_2BF_4$: C, 62.86; H, 5.38; N, 1.56. Found : C, 62.30; H, 5.04; N, 1.25.

{Pd(PPh$_3$)$_2$(η^3-CH$_2$C[C(CO$_2$Me)=CMe-(NH^{i}Pr)]CH$_2$)}(PF$_6$) (4b). Refer to 4a for the procedure. The reaction of **2** (100 mg, 0.12 mmol) and **1b** (20 mg, 0.15 mmol) gave yellow solid product in 76% isolated yield (90 mg). IR (KBr pallet) ν_{CO} 1638 cm^{-1}; ^{31}P NMR ($CDCl_3$, 300 MHz) δ 24.53; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15 (6H, d, J_{HH} = 6.4 Hz, CH(C$\underline{H}_3$)$_2$), 2.04 (3H, C$\underline{H}_3$), 3.14 (3H, s, OC$\underline{H}_3$), 3.68 (5H, m, br, C$\underline{H}_2$(allyl), C$\underline{H}$(CH$_3$)$_2$), 6.82-7.64 (30H, m, phenyl H), 10.09 (1H, d, J_{HH} = 2.0 Hz, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 17.7 (C$\underline{H}_3$), 23.5 (s, (C$\underline{H}_3$)$_2$CH), 45.3 ((CH$_3$)$_2$C$\underline{H}$), 50.9 (OC$\underline{H}_3$), 78.5 (t, J_{CP} = 15.7 Hz, C_t), 91.2 (MeC=C), 128.7, 128.9, 130.1, 130.7, 131.1, 133.7 (phosphino phenyl C), 141.5 (C_c), 164.0 (MeC=C), 168.8 ($\underline{C}$O$_2$Me). MS (FAB, m/z): 826 (M^+-PF_6). Anal. Calcd for $PdC_{47}H_{48}NO_2P_3F_6{\cdot}CH_2CH_2$: C, 55.43; H, 4.75; N, 1.35. Found : C, 54.01; H, 4.63; N, 1.11.

{Pt(PPh$_3$)$_2$(η^3-CH$_2$C[C(COMe)=CMe-(NH^{i}Pr)]CH$_2$)}(PF$_6$) (4a'). The reaction of **3** (240 mg, 0.28 mmol) and equimolar amounts of **1a** produced **4a'** in 82% (220 mg). ^{31}P NMR ($CDCl_3$, 300 MHz) δ 18.1 (J_{PPt} = 3828 Hz,); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00 (6H, d, J_{HH} = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 2.13, 2.15 (3H, 3H, s, s, C$\underline{H}_3$), 3.33 (2H, br, H_{syn}), 3.45 (2H, dd, J_{HP} = 8 Hz, J_{HPt} = 40.8 Hz, H_{anti}), 3.77 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 7.03-7.76 (30H, m, phenyl H), 12.5 (1H, d, J_{HH} = 2.2 Hz, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 15.2, 23.4

($\underline{C}H_3$), 30.6 ($\underline{C}H_2$), 45.4 ($CO\underline{C}H_3$), 69.6 (d, J_{CP} = 34 Hz, J_{CPt} = 105 Hz, C_t), 103.7 (J_{CPt} = 30 Hz, C_γ), 128.0-133.9 (phosphino phenyl C), 143.5 (t, J_{CP} = 4 Hz, J_{CPt} = 20.2 Hz, C_c), 165.1 (N$\underline{C}$=C), 192.4 ($\underline{C}$OMe). MS (FAB, m/z): 899 (M^+-BF_4). Anal. Calcd for $PtC_{47}H_{48}NOP_2BF_4$: C, 57.20; H, 4.90; N, 1.42. Found : C, 56.78; H, 4.04; N, 1.20.

{Pt(PPh$_3$)$_2$(η^3-CH$_2$C[C(CO$_2$Me)=CMe-(NH^{i}Pr)]CH$_2$)}(BF$_4$) (4b'). Complex **3** was first prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^3-CHCCH$_2$) (300 mg, 0.36 mmol) and $AgBF_4$ (69 mg, 0.36 mmol) in situ. The reaction of **3** and **1b** (0.36 mmol) basically followed the procedure as used for the preparation of **4a** produced **4b'** in 77% isolated yields (272 mg). Colorless single crystals were obtained by recrysatallization from CH_2CH_2/benzene. IR (KBr pallet) ν_{CO} 1634 cm^{-1} $\nu_{C=C}$ 1580 cm^{-1}; ^{31}P NMR ($CDCl_3$, 300 MHz) δ 19.6 (J_{PPt} = 3845 Hz,); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (6H, d, J_{HH} = 6.3 Hz, CH($C\underline{H}_3$)$_2$), 2.20 (3H, J_{HPt} = 7.2 Hz, $C\underline{H}_3$), 3.10 (2H, d, J_{HH} = 8.6 Hz, J_{HPt} = 42 Hz, H_{anti}), 3.20 (3H, s, $OC\underline{H}_3$), 3.63 (2H, br, H_{syn}), 3.77 (1H, dhep, J_{HH} = 6.3, 8.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 7.0-7.6 (30H, m, phenyl H), 10.4 (1H, d, J_{HH} = 8.0 Hz, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 15.1 ($\underline{C}H_3$), 22.6 (s, (CH$_3$)$_2\underline{C}$H), 45.4 (dd, J_{CP} = 5.8, 14.2 Hz, (CH$_3$)$_2\underline{C}$H), 50.9 ($O\underline{C}H_3$), 67.6 (d, J_{CP} = 32 Hz, J_{CPt} = 100 Hz, C_t), 91.6 (J_{CPt} = 27 Hz, MeC=$\underline{C}$), 128.4-133.4 (phosphino phenyl C), 140.6 (t, J_{CP} = 2.9 Hz, J_{CPt} = 18.4 Hz, C_c), 165.0 (J_{CPt} = 19.0 Hz, Me$\underline{C}$=C), 169.1 (J_{CPt} = 11 Hz, $\underline{C}O_2$Me). Anal. Calcd for $PtC_{47}H_{48}NO_2P_2BF_4$: C, 56.29; H, 4.83; N, 1.40. Found : C, 55.74; H, 4.91; N, 1.12.

3-carboxymethyl-2-methyl-4-methylene-N-isopropyldihydropyrrole (5b). ^{1}H NMR (C_6D_6, 200 MHz) δ 1.13 (6H, d, J_{HH} = 6.5 Hz, $C\underline{H}_3$), 2.31 (3H, s, $C\underline{H}_3$), 3.61 (3H, s, $OC\underline{H}_3$), 4.01 (1H, m, J_{HH} = 6.5 Hz, C$\underline{H}$), 4.18 (2H, t, J_{HH} = 3.4 Hz, C$\underline{H}_2$), 4.52, 5.10 (1H, 1H, dt, J_{HH} = 1.5, 3.4 Hz, =C$\underline{H}_2$).

3-acetyl-2,4-dimethyl-N-isopropyldihydropyrrole (6a). A solution that contained 4a (30 mg) in 2 mL of chloroform was heated at 50 ℃ for 24 h. The solution was then chromatographed on alumina and eluted with Et_2O. Compound **6a** was obtained in 75% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.34 (6H, d, J_{HH} = 6.6 Hz, CH($C\underline{H}_3$)$_2$), 2.38, 2.47 (3H, s, s, $C\underline{H}_3$), 4.28 (1H, m, J_{HH} = 6.6 Hz, $C\underline{H}$(CH$_3$)$_2$), 6.38 (1H, s, =C$\underline{H}$).

3-carboxymethyl-2,4-dimethyl-N-isopropylpyrrole (6b). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.34 (6H, d, J_{HH} = 6.6 Hz, $C\underline{H}_3$), 2.19 (3H, s, $C\underline{H}_3$), 2.48 (3H, s, $C\underline{H}_3$), 3.76 (3H, s, $OC\underline{H}_3$), 4.27 (1H, m, J_{HH} = 6.6 Hz, $C\underline{H}_2$), 6.38 (1H, s, =C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 300 Hz) 11.1, 12.8, 23.2, 46.6, 50.3, 114.0, 120.4, 128.4, 132.0, 166.9; HRMS: calcd for $C_{11}H_{17}NO_2$ (M^+) 194.1181, found 194.1180.

4.3. X-ray crystallographic Analysis.

basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogenic atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and the C–H distance of 1.0 Å; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from ref 15. Computing programs are from the NRCC SDP VAX package [16]. Crystallographic data, selected bond parameters of **4b'** are collected in Tables 2 and 3. UK on request, quoting the deposition number 135924.

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