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Addition of the alkenyl C–H bond of enamines to η^3-allenyl/propargyl complexes leading to the formation of pyrrole derivatives

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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 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 the C_3H_3 moiety.

Keywords: Enamine; Alkenylation; Pyrrole

1. Introduction

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 for the development of novel ways of 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 subject 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, compound **3** activates a phenyl C–H bond in NMe_2Ph to allow 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 of metal complexes of allenyl/propargyl. The insertion of η^3-C_3H_3 to an enamine C–H bond affords a diene 'skeleton' which allows incorporation of an amino functionality to form the pyrrole derivatives.

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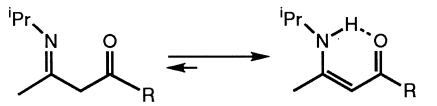
2. Results and discussion

The enamines Me(NH^{i}Pr)C=CHR [R = COMe (**1a**), CO_2Me (**1b**)] have been prepared by the reactions of α,γ-diketone or ketoester methane, respectively, with ^{i}PrNH$_2$ [10]. The NMR data for compounds **1a** and **1b** indicate that tautomerization 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** (1)

Previous studies have shown that amines and amino derivatives with active hydrogen are prone to undergo 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 (N-TMM represents the azatrimethylenemethane complexes $M[CH_2C(NR)CH_2]$) [11]. However, heating a mixture of compounds **2** and **1b** at 50°C was found to generate the pyrrole derivatives. Further investigation shows that reactions of equimolar amounts of compound **2** and enamine at 25°C 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 enamine–allyl complexes of the formula of $Pd(PPh_3)_2\{\eta^3\text{-}CH_2C$-

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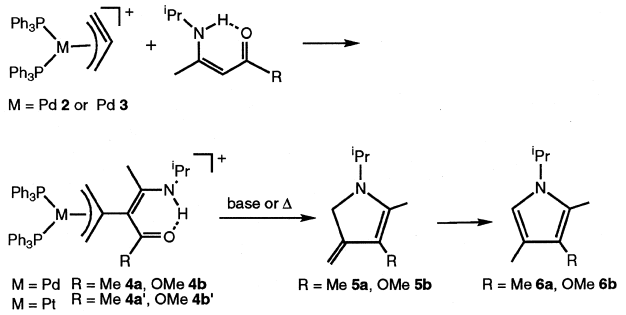

Scheme 1.

$[C(COR)CMe(NH^iPr)]CH_2\}^+$ [R = Me (**4a**), OMe (**4b**)] with yields of over 75%. Complexes **4a** and **4b** were characterized mainly by NMR techniques and elemental analysis. By heating the reaction solutions of complexes **4a** and **4b** to 50°C, or treating them with base, yielded the pyrrole derivatives **6a** and **6b**, respectively (Scheme 1).

The analogous reactions of $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**3**) with compound **1a** or **1b** produced $\{Pt(PPh_3)_2(\eta^3\text{-}CH_2C[C(COR)=CMe(NH^iPr)]CH_2)\}(BF_4)$ [R = Me (**4a′**), OMe (**4b′**)], also in very good yields. The enamine–allyl platinum complexes could alternatively be formed from the reactions of *trans*-$Pt(Br)(PPh_3)_2(\eta^1\text{-}CHCCH_2)$ and enamine at 25°C, but with longer reaction time. Single-crystal X-ray crystallography provides the authentic molecular structure of **4b′**. Fig. 1 shows its ORTEP drawing. The length of C2–C4 is 1.46(2) Å, a typical C_{sp^2}–C_{sp^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 is consistent with the η^3-allyl characteristic and somewhat approaches that of the η^3-trimethylenemethane species [7,12]. This 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, which 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)°. The single crystals of compound **4b′** were obtained by recrystallization in CH_2Cl_2–Et_2O solution. Crystal data: orthorhombic $P2_12_12_1$ $a = 11.100(5)$ Å, $b = 17.764(4)$ Å, $c = 21.951(4)$ Å, $V = 4328(2)$ Å^3, Mo Kα radiation $\lambda = 0.7107$ Å, $Z = 4$, $\mu = 3.398$ mm^{-1}, 5490 total reflections, 3032 observed reflections ($I > 2.0\sigma(I)$), $R = 0.044$, $R_w = 0.036$.

Ring closure in compounds **4a** and **4b** could be accomplished by heating or treating with base as well, except that cyclization of compound **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 furan formation from an enolate–allyl complex [13].

3. Conclusions

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

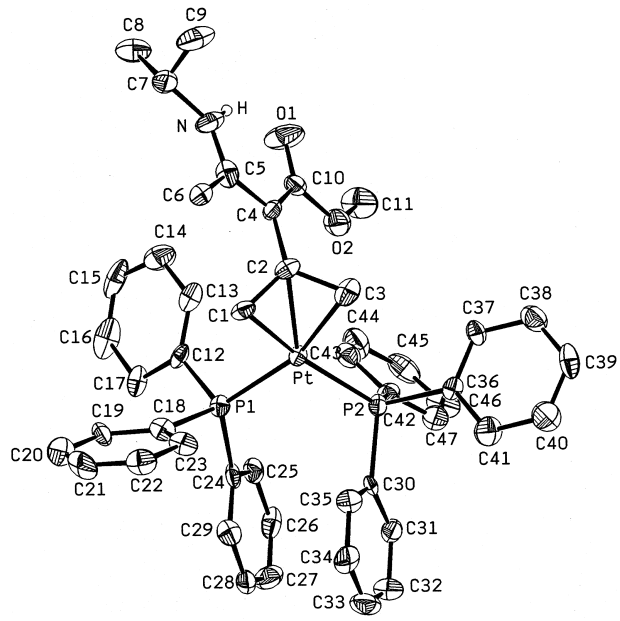

Fig. 1. ORTEP drawing of $\{Pt(PPh_3)_2(\eta^3\text{-}CH_2C[C(CO_2Me)\text{-}CMe(NH^iPr)]CH_2)\}(BF_4)$ (**4b′**) with 50% probability ellipsoids. All hydrogen atoms except the N-bound one are omitted for clarity. Selected bond distances (Å) and angles (°): Pt–P1 2.298(4), Pt–P2 2.300(3), Pt–C1 2.17(1), Pt–C2 2.24(1), Pt–C3 2.19(1), C1–C2 1.40(2), C2–C3 1.45(2), C2–C4 1.46(2), C4–C5 1.44(2), C4–C10 1.41(2), C5–N 1.32(2), C10–O1 1.22(2); ∠P1–Pt–P2 100.3(1), ∠C1–Pt–C3 66.2(5), ∠C1–C2–C3 113(1), ∠C1–C2–C4 122(1), ∠C3–C2–C4 125(1), ∠C5–C4–C10 116(1), ∠C5–C4–C2 118(1), ∠C2–C4–C10 126(1), ∠C4–C5–N 120(1), ∠C4–C10–O1 130(1).

4. Experimental

4.1. General

Commercially available reagents were purchased and used without purification unless necessary. Solvents were dried using standard procedures. All reactions and other manipulations 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 (MS) data were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer.

4.2. Synthesis and characterization

4.2.1. $\{Pd(PPh_3)_2(\eta^3\text{-}CH_2C[C(COMe)=CMe(NH^iPr)]\text{-}CH_2)\}(BF_4)$ (**4a**)

The reaction of compound **2** (300 mg, 0.39 mmol) and (MeOC)HC=CMe(NH^iPr) (**1a**) (55 μl, 0.039 mmol) was

carried out in 20 ml of predried CH_2Cl_2 at −30°C. After stirring for 90 min, the solution was concentrated to 2 ml. Addition of 20 ml of dried Et_2O gave a yellow solid product. Recrystallization resulted in compound **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, CH_3), 2.00 (6H, d, J_{HH} = 6.9 Hz, CH(CH_3)$_2$), 3.50 (2H, m, br, H_{anti}), 3.69 (1H, m, CH(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, NH). ^{13}C NMR (CD_3CN, 300 MHz): δ 18.4, 23.7 (*C*H$_3$), 30.5 (*C*H$_2$), 46.2 (CO*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*C*=C), 193.7 (*C*OMe). MS (FAB, *m*/*z*): 810 ($M^+ - BF_4$). *Anal*. Calc. 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%.

*4.2.2. {Pd(PPh$_3$)$_2$(η^3-CH$_2$C[C(CO$_2$Me)=CMe(NH^{i}Pr)]-CH$_2$)}(PF$_6$) (**4b**)*

Refer to compound **4a** for the procedure. The reaction of compounds **2** (100 mg, 0.12 mmol) and **1b** (20 mg, 0.15 mmol) gave a yellow solid product in 76% isolated yield (90 mg). IR (KBr) (cm^{-1}): ν_{CO} 1638. ^{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(CH_3)$_2$), 2.04 (3H, CH_3), 3.14 (3H, s, OCH_3), 3.68 (5H, m, br, CH_2(allyl), CH(CH$_3$)$_2$), 6.82–7.64 (30H, m, phenyl H), 10.09 (1H, d, J_{HH} = 2.0 Hz, NH). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 17.7 (*C*H$_3$), 23.5 (s, (*C*H$_3$)$_2$CH), 45.3 ((CH$_3$)$_2$*C*H), 50.9 (O*C*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 (Me*C*=C), 168.8 (*C*O$_2$Me). MS (FAB, *m*/*z*): 826 ($M^+ - PF_6$). *Anal*. Calc. for $PdC_{47}H_{48}NO_2P_3F_6.CH_2Cl_2$: C, 55.43; H, 4.75; N, 1.35. Found: C, 54.01; H, 4.63; N, 1.11%.

*4.2.3. {Pt(PPh$_3$)$_2$(η^3-CH$_2$C[C(COMe)=CMe(NH^{i}Pr)]-CH$_2$)}(PF$_6$) (**4a′**)*

The reaction of compound **3** (240 mg, 0.28 mmol) and an equimolar amount of compound **1a** produced compound **4a′** in 82% yield (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(CH_3)$_2$), 2.13, 2.15 (3H, 3H, s, s, CH_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, CH(CH$_3$)$_2$), 7.03–7.76 (30H, m, phenyl H), 12.5 (1H, d, J_{HH} = 2.2 Hz, NH). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 15.2, 23.4 (*C*H$_3$), 30.6 (*C*H$_2$), 45.4 (CO*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*C*=C), 192.4 (*C*OMe). MS (FAB, *m*/*z*): 899 ($M^+ - BF_4$). *Anal*. Calc. 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%.

*4.2.4. {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 compounds **3** and **1b** (0.36 mmol) basically followed the procedure used for the preparation of compound **4a** and produced **4b′** in 77% isolated yields (272 mg). Colourless single crystals were obtained by recrystallization from CH_2CH_2–benzene. IR (KBr) (cm^{-1}): ν_{CO} 1634, $\nu_{C=C}$ 1580. ^{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(CH_3)$_2$), 2.20 (3H, J_{HPt} = 7.2 Hz, CH_3), 3.10 (2H, d, J_{HH} = 8.6 Hz, J_{HPt} = 42 Hz, H_{anti}), 3.20 (3H, s, OCH_3), 3.63 (2H, br, H_{syn}), 3.77 (1H, dhep, J_{HH} = 6.3, 8.0 Hz, CH(CH$_3$)$_2$), 7.0–7.6 (30H, m, phenyl H), 10.4 (1H, d, J_{HH} = 8.0 Hz, NH). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 15.1 (*C*H$_3$), 22.6 (s, (*C*H$_3$)$_2$CH), 45.4 (dd, J_{CP} = 5.8, 14.2 Hz, (CH$_3$)$_2$*C*H), 50.9 (O*C*H$_3$), 67.6 (d, J_{CP} = 32 Hz, J_{CPt} = 100 Hz, C_t), 91.6 (J_{CPt} = 27 Hz, MeC=*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*C*=C), 169.1 (J_{CPt} = 11 Hz, *C*O$_2$Me). *Anal*. Calc. 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%.

*4.2.5. 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, CH_3), 2.31 (3H, s, CH_3), 3.61 (3H, s, OCH_3), 4.01 (1H, m, J_{HH} = 6.5 Hz, CH), 4.18 (2H, t, J_{HH} = 3.4 Hz, CH_2), 4.52, 5.10 (1H, 1H, dt, J_{HH} = 1.5, 3.4 Hz, =CH_2).

*4.2.6. 3-Acetyl-2,4-dimethyl-N-isopropyldihydropyrrole (**6a**)*

A solution that contained compound **4a** (30 mg) in 2 ml of chloroform was heated at 50°C 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(CH_3)$_2$), 2.38, 2.47 (3H, s, s, CH_3), 4.28 (1H, m, J_{HH} = 6.6 Hz, CH(CH$_3$)$_2$), 6.38 (1H, s, =CH).

*4.2.7. 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, CH_3), 2.19 (3H, s, CH_3), 2.48 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 4.27 (1H, m, J_{HH} = 6.6 Hz, CH_2), 6.38 (1H, s, =CH). ^{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: calc. for $C_{11}H_{17}NO_2$ (M^+) 194.1181; found 194.1180.

4.3. X-ray crystallographic analysis

Diffraction data were measured at 298 K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the 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 isotropic 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 international tables [14]. Computing programs are from the NRCC SDP VAX package [15]. Detailed data of compound **4b′**are supplied in the supplementary material.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), on request, quoting deposition number 135924.

Acknowledgements

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