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Communications

Interconversion of η^1-Propargyl, η^1-Allenyl, and η^3-Propargyl/Allenyl Ligands on Platinum. Synthesis, Structure, and Reactivity of $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$

Patrick W. Blosser, David G. Schimpff, Judith C. Gallucci, and Andrew Wojcicki*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Summary: The η^3*-propargyl/allenyl complex* $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (**4**)*, formed by reaction of trans-* $(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ *with* AgO_3SCF_3 *or* $(Ph_3P)_2Pt(\eta^2\text{-}PhC{\equiv}CCH_2OMe)$ *with* $BF_3{\cdot}OEt_2$*, reacts with* Br^- *to yield 9:1 cis-/trans-*$(Ph_3P)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$*, with excess* PMe_3 *to give* $[(Me_3P)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$*, and with CO to afford 1:1* $[trans\text{-}(Ph_3P)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)]^+/[trans\text{-}(Ph_3P)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$*. With* Et_2NH*, ROH (R = Me, Et), and* $CH(CO_2Me)_2^-$*, 4 undergoes nucleophilic addition to the central C atom with transfer of hydrogen to the CPh atom of* η^3*-*CH_2CCPh *to produce* η^3*-allyl complexes as single syn or anti isomers.*

The chemistry of transition-metal propargyl and allenyl complexes has been under investigation for over two decades.[1] These complexes are useful starting materials for the synthesis of compounds with five-membered rings[2] and versatile templates for the construction of transition-metal clusters.[3] Whereas η^1-propargyl and η^1-allenyl complexes have been known since the 1960s,[4] only recently have η^3 bonding modes for these ligands been realized[5-9] or proposed to be present.[10] The reports of $[(\eta^6\text{-}C_6Me_5H)(CO)_2Mo(\eta^3\text{-}CH_2CCH)]^+$ by Krivykh[5] and $Cp_2ZrMe(\eta^3\text{-}CH_2CCPh)$ by us[9] have provided X-ray crystallographic evidence for this rare mode of propargyl/allenyl ligand attachment. In a recent communication, Casey[7] described the preparation of $[(C_5Me_5)(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CMe)]^+$ and its reactions with soft nucleophiles to produce rhenacyclobutene complexes. We have been independently investigating the chemistry of Pt(II) propargyl and allenyl complexes[11] and communicate herein the synthesis of $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (**4**), an X-ray analysis of its structure, and its reaction chemistry, which demonstrates the propensity of the η^3 ligand to undergo a decrease of hapticity in forming η^1-propargyl or η^1-allenyl complexes. Concurrent with our research, Chen[8] prepared the η^3-CH_2CCH analogue of **4** and demonstrated its versatility as a precursor to β-substituted η^3-allyl complexes. We now report that reactions of **4** with ROH (R

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= Me, Et), Et_2NH, and $CH((CO_2Me)_2)^-$ yield only one stereoisomer of a β-substitued η^3-allyl complex in each case, and with $CH((CO_2Me)_2)^-$ the product is a substituted η^3-trimethylenemethane zwitterionic complex.

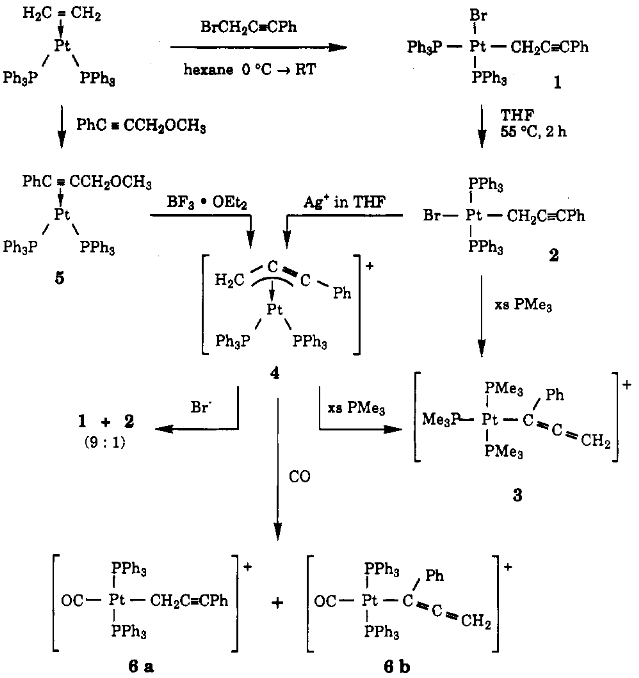
Dropwise addition of phenylpropargyl bromide to a stirred suspension of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ in hexane at 0 °C followed by warming to room temperature over 2 h yields yellow *cis*-$(Ph_3P)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ (**1**; 98%). **1** is readily converted to the yellow *trans*-$(Ph_3P)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ (**2**), by heating at 55 °C in THF for 2 h. The CH_2 resonances (in CD_2Cl_2) in the ^1H NMR (δ 1.39 (t, J_{HP} = 8.1 Hz, J_{HPt} = 103 Hz)) and ^{13}C NMR (δ −5.5 (tt, $^1J_{CH}$ = 140 Hz, $^2J_{CP}$ = 3.9 Hz, $^1J_{CPt}$ = 637 Hz)) spectra of **2** clearly indicate the $\eta^1\text{-}CH_2C{\equiv}CPh$ mode of bonding.[12] The only other 16-electron transition-metal η^1-propargyls, *viz.* Pd(II) complexes with bulky propargylic γ-substituents, have been reported by Boersma.[13]

Attempts to substitute PMe_3 for PPh_3 in **2** resulted not only in phosphine exchange but also in tautomerization of the η^1-phenylpropargyl to an α-substituted η^1-phenylallenyl group. Following anion metathesis, $[(Me_3P)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ (**3**) was isolated in 78% yield, and its structure was confirmed by single-crystal X-ray diffraction techniques.[14] Transformation of the γ-substituted η^1-propargyl to an α-substituted η^1-allenyl rules out a possible mechanism involving a 1,3-hydrogen shift. Instead, a 1,3-platinum sigmatropic rearrangement is the likely mechanism for the observed isomerization. In an effort to support this hypothesis, we sought methods of preparing a viable intermediate.

When **2** was reacted with 1 equiv of AgO_3SCF_3 in THF at room temperature, immediate precipitation of AgBr occurred with formation of $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (**4**), which was isolated as the beige triflate salt in 96% yield.[15] Unlike $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCH)]^+$, reported by Chen[8] to be unstable at ambient temperatures, **4** is thermally stable under argon for at least 1 day at room temperature in $CHCl_3$, CH_2Cl_2, or THF solution and stable as a solid for days in air and for months under argon. An alternative route to **4** is provided by treatment of $(Ph_3P)_2Pt(\eta^2\text{-}PhC{\equiv}CCH_2OMe)$ (**5**) with $BF_3{\cdot}OEt_2$ (*cf.* Scheme I). Owing to the ready accessibility of **5** by reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with $PhC{\equiv}CCH_2OMe$, this methodology may provide an alternative route to differently substituted analogues of **4**.

The structure of the cation **4** of $4(O_3SCF_3){\cdot}CH_2Cl_2$ is presented in Figure 1.[16] The metrical data associated with the $\eta^3\text{-}CH_2CCPh$ ligand and its attachment to the metal are similar to those reported[5] for $[(\eta^6\text{-}C_6Me_5H)(CO)_2Mo(\eta^3\text{-}CH_2CCH)]^+$. For both cations, the M–C(η^3-propargyl) bond distances follow the order M–C(2) < M–C(1), M–C(3), and the C(1)–C(2) and C(2)–C(3) bond lengths are respectively 1.39(2) and 1.23(1) Å for **4** and 1.380(4) and 1.236(4) Å for the Mo complex. These data are interpreted in terms of greater contribution from an η^3-propargyl than an η^3-allenyl resonance structure for both compounds. However, the value of $^1J_{C(1)H}$ of 170 Hz for **4** indicates that the η^3-allenyl representation is also important.

Scheme I



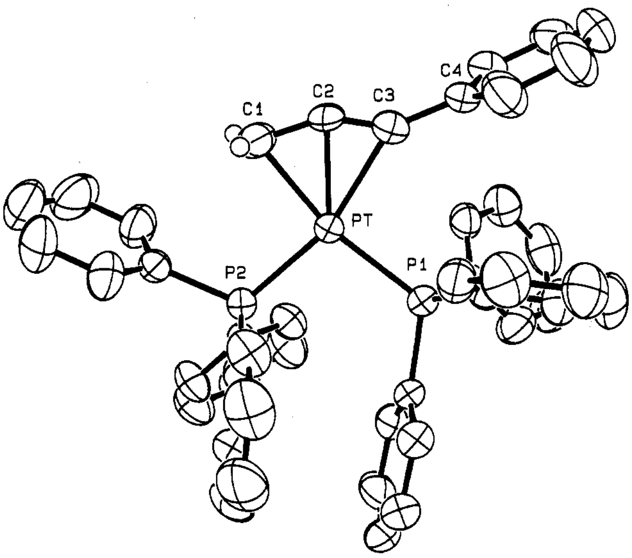


Figure 1. ORTEP plot of **4**. Selected bond distances (Å) and angles (deg): Pt–C(1) = 2.186(11), Pt–C(2) = 2.150(9), Pt–C(3) = 2.273(10), C(1)–C(2) = 1.39(2), C(2)–C(3) = 1.23(1); C(1)–C(2)–C(3) = 152(1), C(2)–C(3)–C(4) = 148(1).

The facile interconversion between η^3 and η^1 bonding modes for transition-metal allyl complexes is well documented and represents an important intramolecular process in olefin isomerization and other related catalytic

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[12] For ^1H and ^{13}C NMR spectra of transition-metal η^1-propargyl complexes see, e.g.: Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185 and references therein.

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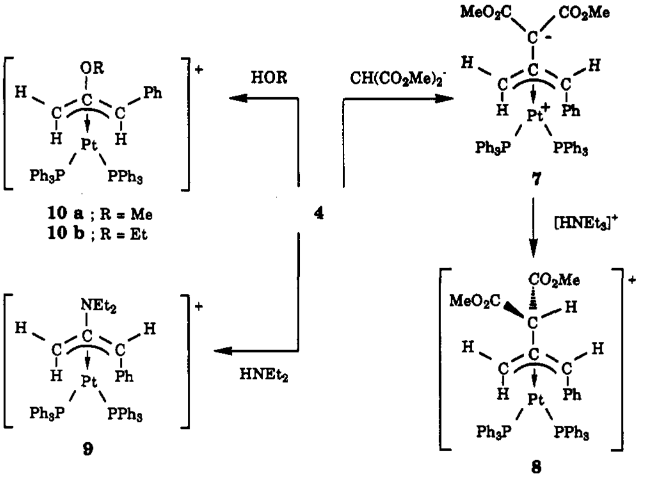
[14] The X-ray analysis of **3** will be published in our full paper: Blosser, P. W.; Gallucci, J. C.; Schimpff, D. G.; Wojcicki, A.; Calligaris, M.; Faleschini, P. To be submitted for publication.

[15] Selected spectral data for $4(O_3SCF_3)$ ($CDCl_3$): ^1H NMR δ 7.5–6.5 (m, 35 H, Ph), 2.74 (d, 2 H, J_{HP} = 6.8 Hz, J_{HPt} = 29.9 Hz, CH_2); ^{13}C NMR δ 135–128 (m, 7 Ph), 102.1 (dd, J_{CP} = 47 Hz, J_{CP} = 1.5 Hz, J_{CPt} = 93 Hz, *C*Ph), 97.3 (dd, J_{CP} = 4.8 Hz, J_{CP} = 3.2 Hz, J_{CPt} = 63 Hz, CH_2C), 48.3 (td, $^1J_{CH}$ = 170 Hz, J_{CP} = 37 Hz, J_{CPt} = 126 Hz, CH_2); $^{31}P\{^1H\}$ NMR δ 15.4 (d, J_{PP} = 18.7 Hz, J_{PPt} = 3785 Hz), 10.5 (d, J_{PP} = 18.7 Hz, J_{PPt} = 4285 Hz); $^{19}F\{^1H\}$ NMR δ −78.9 (s).

[16] Crystal data for $4(O_3SCF_3){\cdot}CH_2Cl_2$: $C_{46}H_{37}F_3O_3P_2PtS{\cdot}CH_2Cl_2$, monoclinic, $P2_1/n$; a = 10.678(3) Å, b = 19.633(4) Å, c = 21.427(2) Å, β = 92.69(1)°, V = 4487(1) Å^3, Z = 4, D_{calc} = 1.58 g cm^{-3}. The data were collected at ambient temperature with Mo Kα radiation: μ = 34.44 cm^{-1}, 2θ limits 4–55°, 484 variables refined with 5797 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ to $R(F)$ = 0.047 and $R_w(F)$ = 0.056.

Scheme II



processes.[17] However, such interconversions for transition-metal propargyl and allenyl complexes have essentially been elusive. Our recent report of the rapid exchange of η^1 and η^3 bonding modes for the two CH_2CCPh ligands in $Cp_2Zr(CH_2CCPh)_2$[9] and Casey's report[18] of the role of η^1- to η^3-propargyl rearrangement in promoting migration of a vinyl ligand to coordinated CO are two important exceptions.

The reactions of 4 with PMe_3, Br^-, and CO (Scheme I) are the first reported reactions of an η^3-propargyl/allenyl complex in which addition occurs at the metal to result in decreased hapticity for this η^3-hydrocarbyl ligand. The reaction of 4 with Br^- in THF yields a mixture of the η^1-propargyl complexes 1 and 2 (9:1) in >95% NMR yield.[19] 4 can likewise be cleanly converted to the η^1-allenyl complex 3 by treatment with excess PMe_3. A most interesting reaction of 4 is that with CO to form a roughly 1:1 mixture of [*trans*-$(Ph_3P)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)$]$O_3SCF_3$ (**6a**) and [*trans*-$(Ph_3P)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2)$]$O_3SCF_3$ (**6b**). Efforts to separate **6a** and **6b**, or to convert the mixture to one isomer by heating, repeatedly resulted in decomposition. A sharp contrast of spectroscopic features for the two isomers is provided by both ^1H and $^{13}C\{^1H\}$ NMR. The methylene protons of **6a** in CD_2Cl_2 resonate at δ 1.98 as compared to δ 3.65 for **6b**. In the $^{13}C\{^1H\}$ NMR spectrum, resonances at δ 7.1, 86.1, and 92.2 are respectively assigned to the CH_2, $-C{\equiv}$, and ${\equiv}CPh$ carbons of **6a**, while signals at δ 72.9, 203.1, and 101.5 are similarly assigned to the CH_2, $={C}=$, and $=CPh$ carbons of **6b**. The foregoing transformations of 4 to both η^1-propargyl and η^1-allenyl complexes support the hypothesis that η^3-propargyl/allenyl intermediates play a major role in propargyl/allenyl tautomerizations.

Consistent with the report by Chen,[8] 4 adds a variety of nucleophiles at the central carbon atom of the η^3-propargyl ligand with resultant conversion to η^3-allyl complexes (Scheme II). Its behavior toward $Na[CH(CO_2Me)_2]$ provides a remarkable example of the extreme propensity of 4 to react in this manner. Mixing of 4 with an equimolar quantity of $Na[CH(CO_2Me)_2]$ in THF leads to formation of the zwitterionic η^3-allyl complex 7 in 70% isolated yield.[20] The observation of only one methyl resonance in the ^1H NMR spectrum and only one resonance for each of the methyl and ester carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum indicates that this product is not a platinacyclobutane–β-alkylidene complex. 7 may be expected to undergo reactions similar to those of Pd(II) zwitterionic trimethylenemethane complexes, which have proven utility in organic synthesis,[21] and such cycloaddition reactions are currently under investigation. 7 is readily converted to the cationic $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(CH(CO_2Me)_2)CHPh)]BPh_4$ (8) by protonation with $[HNEt_3]BPh_4$ in THF.

4 also reacts with Et_2NH and ROH (R = Me, Et) to form β-substituted cationic η^3-allyl complexes **9**, **10a** (R = Me), and **10b** (R = Et), respectively. These nucleophilic additions are accompanied by hydrogen transfer to the *C*Ph carbon atom of the η^3-propargyl/allenyl group. The assignment of structures **7–10** in Scheme II is supported by ^1H NMR spectra of these complexes. In each case, the C*H*Ph protons resonate downfield (δ 4.38–5.59) of typical η^3-allylic protons[22] owing to the deshielding effect of the geminal phenyl substituent.[23] Long-range W-shaped coupling ($^4J_{H_sH_{s'}}$) observed by selective proton decoupling experiments for the two syn protons in **7–9** is absent for **10a** and **10b**. For all the η^3-allyl complexes **7–10** only one isomer, syn or anti, has been detected.

We are currently investigating mechanistic details of these intriguing transformations as well as extensions to Pd(II) chemistry.

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Supplementary Material Available: Text giving experimental procedures, NMR spectroscopic data, and elemental analyses for complexes 1–10 and details of the structure determination of $4(O_3SCF_3)\cdot CH_2Cl_2$, including tables giving details of the data collection and refinement, positional and thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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(17) See, e.g.: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 175. (b) Masters, C. *Homogeneous Transition-metal Catalysis: A Gentle Art*; Chapman and Hall: London, 1981.

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(19) It was not determined whether 2 formed directly by attack of Br^- at Pt or via cis to trans isomerization.

(20) Selected spectral data for 7 (CD_2Cl_2): ^1H NMR δ 7.5–7.0 (m, 35 H, Ph), 5.38 (m, 1 H, C*H*Ph), 4.00 (m, 1 H, H_{syn}), 3.49 (s, 6 H, Me), 2.60 (dd, 1 H, J_{HP} = 11.3 Hz, J_{gem} = 4.2 Hz, J_{HPt} = 55 Hz, H_{anti}); $^{13}C\{^1H\}$ NMR δ 170.7 (s, 2 *C*O_2Me), 149.2 (t, J_{CP} = 3.4 Hz, J_{CPt} = 91 Hz, H_2C*C*), 144–122 (m, 7 Ph), 88.4 (s, =*C*$(CO_2Me)_2$), 70.7 (d, J_{CP} = 47 Hz, J_{CPt} = 227 Hz, *C*HPh), 50.3 (s, 2 Me), 46.6 (d, J_{CP} = 42 Hz, J_{CPt} = 159 Hz, CH_2); $^{31}P\{^1H\}$ NMR δ 20.1 (d, J_{PP} = 3.6 Hz, J_{PPt} = 3359 Hz), 18.6 (d, J_{PP} = 3.6 Hz, J_{PPt} = 3126 Hz).

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