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Reaction of Isocyanides with $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ and the Formation of the Indenyl Complex *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-inden-2-yl})(CNC(CH_3)_3)]^+$

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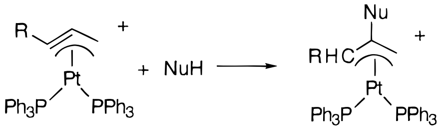
The reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]X$ ($X = CF_3SO_3^-$, BF_4^-, PF_6^-) with CNR ($R = C(CH_3)_3$, CH_2Ph) yields a mixture of the η^1-propargyl and -allenyl complexes *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNR)]^+$ and *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CPh{=}C{=}CH_2)(CNR)]^+$, respectively, in about a 6/1 proportion. Isolation of the pure propargyl complex was possible in several cases ($R = C(CH_3)_3$, $X = CF_3SO_3^-$; $R = CH_2Ph$, $X = BF_4^-$, PF_6^-). In solution the cationic complex *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNC(CH_3)_3)]^+$ rearranges to an indenyl complex which was isolated as the triflate salt *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-inden-2-yl})(CNC(CH_3)_3)]CF_3SO_3$ (**4**). In contrast *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNCH_2Ph)]^+$ does not undergo this rearrangement under similar conditions. The structure of **4**·2THF has been determined by X-ray diffraction techniques.

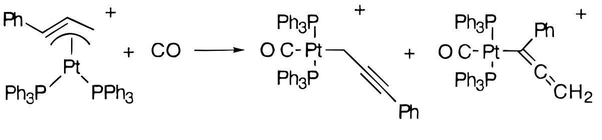
Introduction

Cationic transition-metal η^3-propargyl/allenyl complexes of platinum, $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCR)]^+$, add nucleophiles (NuH) either to the central carbon atom of the η^3-bonded ligand[1−3](eq 1) or to the metal center.[4]



(1)

In the latter reactions, η^1-propargyls (e.g., with Br^-), η^1-allenyls (e.g., with $P(CH_3)_3$), or both (with CO) have been obtained (eq 2). Owing to their cationic nature, these η^1-hydrocarbyl complexes present themselves as potentially valuable substrates for studies of ligand reactions of η^1-propargyl and η^1-allenyl with a variety of nucleophiles.



(2)

Following the observation that CO reacts with $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ to afford a mixture of the η^1-propargyl and η^1-allenyl products,[4] we endeavored to extend this investigation to organic isocyanides. Transition-metal chemistry of organic isocyanides often parallels that of CO; however, significant differences also have been noted.[5]

In this paper we report on reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ with the isocyanides $CNC(CH_3)_3$ and $CNCH_2Ph$. In the course of these investigations we observed that one of the products of the aforementioned reactions, *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNC(CH_3)_3)]^+$, undergoes an unprecedented rearrangement to *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-inden-2-yl})(CNC(CH_3)_3)]^+$, which was characterized by X-ray diffraction analysis as the $CF_3SO_3^-$ salt. We also report studies on this unusual rearrangement.

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of argon or nitrogen using standard procedures.[6] Elemental analyses were performed by Atlantic Microlabs, Inc, Norcross, GA. Infrared spectra were recorded on a Perkin-Elmer Model 1760 or Model 337 spectrophotometer. ^1H, ^2H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-250 or AC200 spectrometer. Signals for the C≡N carbon atom of the cynanide and isocyanide ligands were not observed. 2D XHCORR spectra were obtained on a Bruker AM-500 spectrometer.

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[1] Review: Wojcicki, A. *New J. Chem.* **1994**, *18*, 61.

[2] Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164 and references therein.

[3] (a) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170. (b) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657. (c) Cheng, Y.-C.; Chen, Y.-K.; Huang, T.-M.; Yu, C.-I.; Lee, G.-H.; Wang, Y.; Chen, J.-T. *Organometallics* **1998**, *17*, 2953 and references therein.

[4] Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993.

[5] Selected reviews: (a) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. (b) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

[6] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

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Materials. All solvents were purified by distillation under nitrogen or argon from suitable drying agents. Dichloromethane was distilled from P_4O_{10}, benzene and THF were distilled from sodium benzophenone ketyl, and hexanes were distilled from calcium hydride. Reagents were obtained from various commercial sources and were used as received unless otherwise indicated. Literature procedures were followed to synthesize $C_6H_5C{\equiv}CCH_2Br$,[7] $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]CF_3SO_3$ (**1**),[2] and C_6D_5I.[8]

The deuterated compounds $C_6D_5C{\equiv}CCH_2OH$,[9,10] $C_6D_5C{\equiv}CCH_2Br$,[7] *trans*-$BrPt(PPh_3)_2(\eta^1\text{-}CH_2C{\equiv}CC_6D_5)$,[2] and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCC_6D_5)]CF_3SO_3$[2] were synthesized by the methods referenced for synthesis of the undeuterated counterparts and were characterized by NMR spectroscopy. In each case the ^{1}H NMR spectrum was identical with that for the undeuterated compound except for the absence of the phenyl protons of the CCPh group.

The salts $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]PF_6$ and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]BF_4$ were obtained by substituting $AgPF_6$ or $AgBF_4$, respectively, for $AgCF_3SO_3$ in the synthesis of **1**.[2] Proton and ^{31}P NMR spectra in CD_2Cl_2 for the platinum complex were identical with that of **1**.

Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]CF_3SO_3$ with $CNC(CH_3)_3$ at −30 °C. A solution of 506 mg (0.514 mmol) of **1** in 7 mL of CH_2Cl_2 was cooled to −30 °C, and then 0.57 mL of a 1.0 M solution of $CNC(CH_3)_3$ (1.1 equiv) in benzene was added dropwise. The yellow-brown solution lightened to a paler yellow color. After several minutes hexanes were added slowly to the cold solution until precipitation was complete (ca. 60 mL). The liquid was removed, and the precipitate was washed twice with 5 mL portions of hexanes. The solid was dissolved in 7 mL of CH_2Cl_2 at room temperature, and ether was added dropwise. After 16 mL had been added, the solution was stirred while a white solid slowly precipitated. (In some cases a small amount of a granular white precipitate appeared after the first few milliliters of ether were added but before the main white solid began to form. This granular solid was filtered off before addition of ether to the solution was continued. See below for characterization of this solid.) Further ether was added to the solution in 3−4 mL increments, followed by stirring, until a total of 35 mL had been added. The white solid of *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNC(CH_3)_3)]CF_3SO_3$ (**2**) was collected by filtration, washed several times with ether, and dried under vacuum at 45−50 °C; the yield was 300 mg (0.281 mmol, 55%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.1 (s, $J_{PtP} = 2821$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.9−6.8 (m, Ph), 1.50 (t, $J_{PH} = 9.1$ Hz, $J_{PtH} = 81$ Hz, CH_2), 0.59 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135−128 (m, Ph), 94.0 (s, $J_{PtC} = 74$ Hz, *C*Ph), 83.0 (s, $J_{PtC} = 26$ Hz, $C{\equiv}Ph$), 58.9 (s, $C(CH_3)_3$), 28.4 (s, CH_3), 1.5 (s, $J_{PtC} = 474$ Hz, CH_2). IR (Nujol): $\nu(C{\equiv}N)$ 2213 cm^{-1}. Anal. Calcd for $C_{51}H_{46}F_3NO_3P_2PtS$: C, 57.41; H, 4.35. Found: C, 57.18; H, 4.44.

The filtrate from which **2** was separated was pumped dry to give 138 mg of a yellow-gold solid which, by NMR, was shown to be a mixture of **2** and the η^1-allenyl complex *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CPh{=}C{=}CH_2)(CNC(CH_3)_3)]CF_3SO_3$ (**3**). Attempts to isolate pure **3** were unsuccessful. Spectroscopic data for **3** were obtained from the mixture. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.3 (s, $J_{PtP} = 2716$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.9−6.8 (m, Ph), 3.42 (t, $J_{PH} = 4.2$ Hz, $J_{PtH} = 38$ Hz, CH_2), 0.65 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 203.8 (t, $J_{PC} = 4$ Hz, $C{=}\mathit{C}{=}CH_2$), 134−126 (m, Ph), 100.5 (t, $J_{PC} = 8.6$ Hz, $Ph\mathit{C}{=}C{=}CH_2$), 69.6 (s, $J_{PtC} = 46$ Hz, $PhC{=}C{=}\mathit{C}H_2$), 59.4 (s, $C(CH_3)_3$), 28.7 (s, CH_3). IR (Nujol): $\nu(C{\equiv}N)$ 2208 cm^{-1}, $\nu(C{=}C{=}C)$ 1911 cm^{-1}.

The initial granular solid that sometimes appeared in the above procedure was purified by dissolution in 6 mL of CH_2Cl_2 and reprecipitated by addition of 15 mL of ether. This solid was collected by filtration and washed with 5 mL of a 2/5 CH_2Cl_2/ether mixture. It then was dissolved in CH_2Cl_2, the solution was filtered, the volume was reduced, and hexanes were added to cause precipitation. The white solid was filtered off, washed with hexanes, and dried under vacuum. The yield of *trans*-$[(PPh_3)_2Pt(CNC(CH_3)_3)_2](CF_3SO_3)_2$ varied; the maximum was 35 mg (0.0296 mmol, 5.8%) starting from 506 mg (0.514 mmol) of **1**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 9.80 (s, $J_{PtP} = 2001$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.9−7.4 (br, Ph), 0.68 (s, CH_3). IR (Nujol): $\nu(C{\equiv}N)$ 2239 cm^{-1}. Anal. Calcd for $C_{48}H_{48}F_6N_2O_6P_2PtS_2$: C, 48.69; H, 4.09. Found: C, 48.64; H, 4.14.

Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]CF_3SO_3$ with $CNC(CH_3)_3$ at 55 °C. A sample of 104 mg (0.103 mmol) of **1** was dissolved in 5 mL of CH_2ClCH_2Cl. The solution was cooled to −10 °C, and 0.36 mL of a 0.96 M solution of $CNC(CH_3)_3$ (3.4 equiv) in benzene was added dropwise. The yellow-brown solution lightened to a paler yellow color. The solution was heated in an oil bath at 55−60 °C for 5 h. The solution was cooled to room temperature, and 60 mL of hexanes were added slowly to yield a yellow precipitate. The liquid was removed, and the solid was washed several times with hexanes and then was dried under vacuum. The yield of *trans*-$[(PPh_3)_2Pt(CN)(CNC(CH_3)_3)]CF_3SO_3$ (**5**) was 78 mg (0.080 mmol, 77%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 12.5 (s, $J_{PtP} = 2168$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.6 (br, Ph), 0.69 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.4 (t, $J_{PC} = 6.4$ Hz, ortho Ph), 132.7 (s, para Ph), 129.4 (t, $J_{PC} = 5.8$ Hz, meta Ph), 127.7 (t, $J_{PC} = J_{PtC} = 31.4$ Hz, ipso Ph), 60.9 (s, $C(CH_3)_3$), 28.2 (s, CH_3). IR (Nujol) $\nu(C{\equiv}NC(CH_3)_3)$ 2208 cm^{-1}, $\nu(C{\equiv}N)$ 2151 cm^{-1}. Anal. Calcd for $C_{43}H_{39}F_3N_2O_3P_2PtS$: C, 52.82; H, 4.02. Found: C, 52.21; H, 4.35.

Rearrangement of *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNC(CH_3)_3)]CF_3SO_3$ (2) to *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-inden-}2\text{-yl})(CNC(CH_3)_3)]CF_3SO_3$ (4). A sample of 203 mg (0.191 mmol) of **2** was dissolved in 10 mL of CH_2Cl_2 and heated to reflux. The reaction was monitored by ^{31}P NMR until conversion was complete (ca. 5 h). (Samples taken for NMR analysis were returned to the reaction mixture.) The solvent volume was reduced to 3 mL, and 20 mL of hexanes was added to produce a precipitate. The liquid was discarded, and the remaining solid was washed twice with 3 mL of hexanes. The solid was dissolved in 3 mL of CH_2Cl_2, and 20 mL of ether was added slowly to provide a small amount of a precipitate which was shown by ^{31}P NMR to be a mixture of many components. The precipitate was removed and discarded, and the liquid was pumped to dryness to provide *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-inden-}2\text{-yl})(CNC(CH_3)_3)]CF_3SO_3$ (**4**) as an off-white solid. The yield of **4** was 154 mg (0.144 mmol, 76%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.9 (s, $J_{PtP} = 2730$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.8−6.7 (m, Ph, C_6H_4), 5.97 (t, $J_{PtH} = 31$ Hz, $J_{PH} = 1.5$ Hz, CH), 1.84 (s, $J_{PtH} = 11$ Hz, CH_2), 0.67 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 154.8 (t, $J_{PC} = 11.7$ Hz, $J_{PtC} = 732$ Hz, $Pt\mathit{C}{=}C$), 147.6 (s, $J_{PtC} = 61.2$ Hz, $PtC{=}CH\mathit{C}$), 147.3 (s, $J_{PtC} = 19.7$ Hz, $PtCCH_2\mathit{C}$), 135.0 (t, $J_{PC} = 4.7$ Hz, $C{=}\mathit{C}H$), 134.1 (t, $J_{PC} = 6.3$ Hz, ortho Ph), 131.8 (s, para Ph), 128.9 (t, $J_{PC} = 5.6$ Hz, meta Ph), 128.5 (t, $J_{PC} = J_{PtC} = 29.4$ Hz, ipso Ph), 124.7, 122.1, 121.1, 117.8 (C_6H_4), 58.9 (s, $C(CH_3)_3$), 45.2 (s, $J_{PtC} = 42.0$ Hz, CH_2), 28.4 (s, CH_3). IR (Nujol): $\nu(C{\equiv}N)$ 2208 cm^{-1}. Anal. Calcd for $C_{51}H_{46}F_3NO_3P_2PtS$: C, 57.41; H, 4.35. Found: C, 57.24; H, 4.42.

Investigations of Factors That Might Cause Rearrangement. Investigations of the effects of various substances or factors on the rearrangement of **2** to **4** were carried out by monitoring the ^{31}P NMR spectra of samples in sealed NMR tubes over time. Usually a sample to be tested was dissolved in the solvent, and the solution was divided between two NMR tubes. One was sealed as the control sample, while the test substance was added to the other sample. The NMR tubes were left at room temperature. If no reaction was occurring or if the reaction was proceeding very slowly, the

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[7] Padwa, A.; Meske, M.; Ni, Z. *Tetrahedron* **1995**, *51*, 89.

[8] Joh, T.; Doyama, K.; Fujiwara, K.; Maeshima, K.; Takahashi, S. *Organometallics* **1991**, *10*, 508.

[9] Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.

[10] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

sealed NMR tubes were heated in a 55 °C oil bath for periods of 15−60 min.

Synthesis of $[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CC_6D_5)(CNC(CH_3)_3)]CF_3SO_3$ and Its Rearrangement to the Indenyl Complex. A sample of 0.219 g (0.223 mmol) of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCC_6D_5)]CF_3SO_3$ was taken through the same sequence of steps as those described above for the reaction of **1** with $CNC(CH_3)_3$. Products and their purity were determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The spectra of the η^1-propargyl complex $[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CC_6D_5)(CNC(CH_3)_3)]CF_3SO_3$ were identical to those of the undeuterated complex (**2**) except for the absence of the phenyl protons of the η^1-$CH_2C{\equiv}CPh$ group in the ^1H spectrum in the 6.7−7.0 ppm range.

A sample of $[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CC_6D_5)(CNC(CH_3)_3)]CF_3SO_3$ rearranged to the indenyl complex in CD_2Cl_2 over 2 days at room temperature. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the product were identical with those of the undeuterated compound (**4**) except for the absence of signals in the ^1H spectrum in the 6.7−7.0 ppm range from the C_6H_4 protons on the indenyl group.

Synthesis of *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNCH_2Ph)]PF_6$. The procedure was similar to that for the synthesis of **2** and employed amounts of solvents proportional to the scale of the reaction. Thus, a solution of 282 mg (0.288 mmol) of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]PF_6$ in 4 mL of CH_2Cl_2 was cooled to −30 °C, followed by dropwise addition of 0.58 mL of a 0.5 M solution of $CNCH_2Ph$ in benzene. The solid isolated after addition of excess hexanes was dissolved in 4 mL of CH_2Cl_2. Slow addition of 8 mL of ether gave a white precipitate, which was mainly the desired η^1-propargyl complex. This solid was dissolved in 1.5 mL of CH_2Cl_2 and reprecipitated with 8 mL of ether. The solid was isolated, washed with ether, and pumped dry. The yield of *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(CNCH_2Ph)]PF_6$ was 100 mg (0.091 mmol, 31%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.6 (s, $J_{PtP} = 2792$ Hz, PPh_3), −145.2 (septet, $J_{PF} = 713$ Hz, PF_6^-). ^1H NMR ($CDCl_3$): δ 7.7−6.3 (m, Ph), 3.88 (s, $J_{PtH} = 11$ Hz, $CNCH_2Ph$), 1.55 (t, $J_{PH} = 18$ Hz, $J_{PtH} = 81$ Hz, $CH_2C{\equiv}CPh$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135−124 (m, Ph), 94.6 (s, $J_{PtC} = 71$ Hz, *C*Ph), 82.5 (s, $J_{PtC} = 27$ Hz, $C{\equiv}CPh$), 47.4 (s, CH_2Ph), 0.4 (s, $J_{PtC} = 477$ Hz, $CH_2C{\equiv}C$). IR (Nujol): $\nu(C{\equiv}N)$ 2255 cm^{-1}. Anal. Calcd for $C_{53}H_{44}F_6NP_3Pt$: C, 58.03; H, 4.04. Found: C, 57.85; H, 3.98.

Crystallographic Analysis of *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-}inden\text{-}2\text{-}yl)(CNC(CH_3)_3)]CF_3SO_3\cdot 2THF$ (4·2THF). Clear and colorless crystals of **4·2THF** were grown by slow evaporation of a solution of CH_2Cl_2/THF. All data collection was done at 208 K with a Molecular Structure Corp. low-temperature system. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer indicated an orthorhombic crystal system. On the basis of the systematic absences, the space group possibilities are restricted to *Pnma* and $Pn2_1a$. Unit cell constants were obtained by a least-squares fit of the setting angles for 25 reflections in the 2θ range 21−29° with Mo Kα radiation ($\lambda(K\alpha_1) = 0.709\ 30$ Å). Six standard reflections were measured during data collection and indicated that the crystal was stable. Data reduction was done with the teXsan package.[11] Intensity statistics strongly indicated that the space group was centrosymmetric.

The structure was solved with the Patterson method in SHELXS-86[12] in *Pnma*. Expansion of the model was done with DIRDIF.[13] Full-matrix least-squares refinements based on *F* were performed in teXsan;[11] the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. An analytical absorption correction was applied to the data.[14] With $Z = 4$ in *Pnma*, crystallographic symmetry is imposed on the structure. The Pt complex and the triflate ion each contain a mirror plane. The indenyl ligand lies in the mirror plane and appears to be ordered. The Pt, C(10), N, C(11), and C(12) atoms also lie in the mirror plane. There are two solvent molecules of THF in the asymmetric unit, and each is bisected by a mirror plane. In each THF molecule, only the oxygen atom lies in the mirror plane. Both THF molecules contain large thermal parameters and were refined only isotropically. The hydrogen atoms are included in the model at calculated positions with C−H = 0.98 Å and fixed. The final refinement cycle was based on the 2591 intensities with $I > 3\sigma(I)$ and 329 variables and resulted in final agreement factors of $R = 0.050$ and $R_w = 0.047$. The final difference electron density map contains maximum and minimum peak heights of 1.19 and −1.04 e/Å^3.[13] The largest peaks are in the vicinity of the THF molecules. Neutral atom scattering factors were used[15] and include terms for anomalous dispersion.[16] A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1.

Table 1. Crystal Data and Experimental Details for *trans*-$[(PPh_3)_2Pt(\eta^1\text{-}1H\text{-}inden\text{-}2\text{-}yl)(CNC(CH_3)_3)]CF_3SO_3\cdot 2THF$ (4·2THF)

formula	$C_{59}H_{62}F_3NO_5P_2PtS$
fw	1211.24
cryst syst	orthorhombic
space group	*Pnma*
a, Å	21.029(2)
b, Å	16.287(3)
c, Å	15.851(2)
V, Å^3	5428.9
Z	4
D_{calcd}, g cm^{-3}	1.48
cryst size, mm	0.12 × 0.12 × 0.23
μ(Mo Kα), cm^{-1}	27.31
scan type	ω
scan range, deg (in ω)	1.10
2θ limits, deg	4−50
transmissn factors	0.728−0.764
temp, K	208
scan speed, deg min^{-1} (in ω)	3, with up to 3 rescans
data collected	$+h, +k, +l$
no. of unique data	5335
no. of unique data used in refinement	2591[a]
final no. of variables	329
$R(F)$[b]	0.050
$R_w(F)$[c]	0.047
error in obsn of unit wt, e	1.38

[a] With $F_o^2 > 3\sigma(F_o^2)$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Results and Discussion

The complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]CF_3SO_3$ (**1**) reacts with *tert*-butyl isocyanide in CH_2Cl_2 at or below room temperature to give as the principal products the η^1-propargyl complex **2** and the η^1-allenyl complex **3** in about a 6−8/1 ratio (eq 3). Thus, nucleophilic addition by isocyanide occurs at the platinum center in the manner of the isoelectronic CO but differs in the product ratio, which was about 1/1 with CO.[4] The identification of the products as the η^1-propargyl and -allenyl compounds follows from the ^1H and ^{13}C NMR data. In the ^1H NMR the diagnostic resonances of the η^1-propargyl

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[11] teXsan: Crystal Structure Analysis Package, Version 1.7-2; Molecular Structure Corp., The Woodlands, TX 77381, 1995.

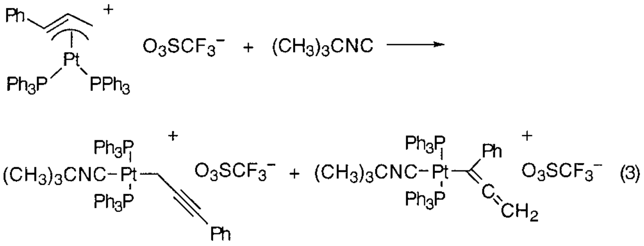
[12] SHELXS86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[13] DIRDIF: Parthasarathi, V.; Beurskens, P. T.; Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860.

[14] De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

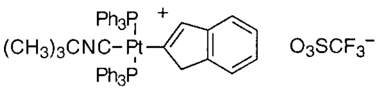
[15] Scattering factors for the non-hydrogen atoms are from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[16] Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Table 4.2.6.8.



and -allenyl CH_2 protons are at 1.50 ppm (J_{PH} = 9.1 Hz, J_{PtH} = 81 Hz) and 3.4 ppm (J_{PH} = 4.2 Hz, J_{PtH} = 38 Hz), respectively. The relative abundance of the two compounds is more easily obtained in the $^{31}P\{^1H\}$ NMR, where the propargyl complex resonates at 19.1 ppm (J_{PtP} = 2821 Hz) and the allenyl complex resonates at 16.3 ppm (J_{PtP} = 2716 Hz). The propargyl product **2** can be isolated in pure form as a white solid by selective precipitation, by addition of diethyl ether to a CH_2Cl_2 solution of the mixture; careful attention to the proportion of the two solvents is essential for success. This separation is also very sensitive to the anion involved. Thus, reactions of the analogous BF_4^- and PF_6^- salts of **1** with $CNC(CH_3)_3$ result in the same product mixture of η^1-propargyl and -allenyl complexes, but all attempts to obtain the pure propargyl product by selective precipitation were unsuccessful. However, the identity of **3** as an η^1-allenyl complex is confirmed by the ^1H and ^{13}C NMR data, which are nearly identical with those of the analogous CO complex $[(PPh_3)_2Pt(CO)(\eta^1\text{-}CPh{=}C{=}CH_2)]^+$,[4] and by the IR band at 1911 cm^{-1} due to the C=C=C group.[17]

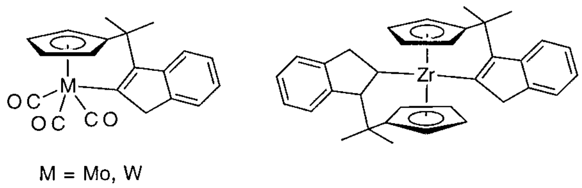
In solution pure **2** undergoes rearrangement to the η^1-indenyl complex **4**. This reaction goes to completion over times varying from a few hours to several days at room temperature. During the conversion, NMR peaks due to another species, presumably an intermediate, grow and then disappear. In the $^{31}P\{^1H\}$ NMR (CD_2Cl_2) a singlet appears at 15.7 ppm (J_{PtP} = 2791 Hz). The proton NMR has a new peak at 0.64 ppm, assigned to the *tert*-butyl group, and a singlet at 3.69 ppm that shows coupling to platinum (J_{PtH} = 20 Hz). No attempt was made to isolate this species due to its low abundance in the mixture.



4

Identification of **4** as a 1*H*-inden-2-yl complex was initially proposed on the basis of NMR data and subsequently confirmed by a crystal structure. Several features of the NMR spectra were particularly important in reaching a structural assignment. In the proton spectrum the CH vinyl proton appears at 5.97 ppm with coupling to both platinum and phosphorus (J_{PtH} = 31 Hz, J_{PH} = 1.5 Hz). The CH_2 protons resonate at 1.84 ppm and show coupling only to platinum (J_{PtH} = 11 Hz). In the ^{13}C NMR spectrum the aromatic region differs substantially from that of the propargyl complex **2**, showing four resonances of equal intensity at 124.7, 122.1, 121.1, and 117.8 ppm which are assigned to the four CH carbon atoms of the six-membered ring. Identification of the remaining indenyl carbon resonances was facilitated by a 2D XHCORR spectrum. This spectrum was particularly important for locating the carbon of the CH group of the five-membered indenyl ring, which has a weak intensity and is at the low-field edge of the phenyl carbon atoms of the PPh_3 groups. The large coupling to platinum (J_{PtC} = 732 Hz) for the resonance at 154.8 ppm identifies the carbon bonded to platinum.

The structure of the cationic platinum complex in **4** is shown in Figure 1, and selected bond lengths and bond angles are presented in Table 2. The coordination geometry around the Pt atom is square planar, and the indenyl ligand lies in a mirror plane in the complex. The C−C bond lengths in the five-membered ring show that the double bond is localized between C(1) and C(2). Relatively few complexes of indene in which a transition metal is σ-bonded to the 2-carbon are known,[18−22] and even fewer, shown below, have only the simple metal−indene bonding found in **4**:[18,19]



The rearrangement of **2** to **4** was unexpected, and the factors that control it are not yet understood. From a variety of studies, the only firm conclusion that can be drawn is that the rearrangement does not occur if any of the allenyl complex **3** is present. Thus, a sample of **2** that contains **3** shows no rearrangement even when heated at 55 °C for several days in dichloromethane in a sealed NMR tube; furthermore, addition of a mixture of **2** and **3** to a sample of **2** that is undergoing rearrangement causes the rearrangement to cease. The rearrangement appears to be solvent-independent, having been observed in dichloromethane, chloroform, THF, and 1,2-dichloroethane. Since silver ion is a possible trace contaminant from the synthesis of **1**, a few grains of AgO_3SCF_3 were added to a solution of **2** in CH_2Cl_2. This does enhance the rate of the rearrangement, but not dramatically. Addition of *p*-toluenesulfonic acid to test the possibility of acid catalysis did increase the rate of loss of **2**, but there were a multitude of products that prevented the clear identification of any **4** among them. Addition of THF saturated with KOH had no effect.

Clearly any mechanistic proposals for the rearrangement are speculative at this time, but catalysis by an electrophile such as in Scheme 1 is a possibility, where H^+ or Ag^+ are two possible candidates for E. This scheme is similar to that for the [3 + 2] cycloaddition

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(17) Wouters, J. M. A.; Klein, R. A.; Elsevier: C. J.; Häming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586.

(18) Alt, H. G.; Han, J. S.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *454*, 165.

(19) Licht, E. H.; Alt, H. G.; Milius, W.; Abu-Orabi, S. *J. Organomet. Chem.* **1998**, *560*, 69.

(20) Chen, H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1990**, 373.

(21) Chen, H.; Fajardo, M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1990**, *389*, C16.

(22) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36.

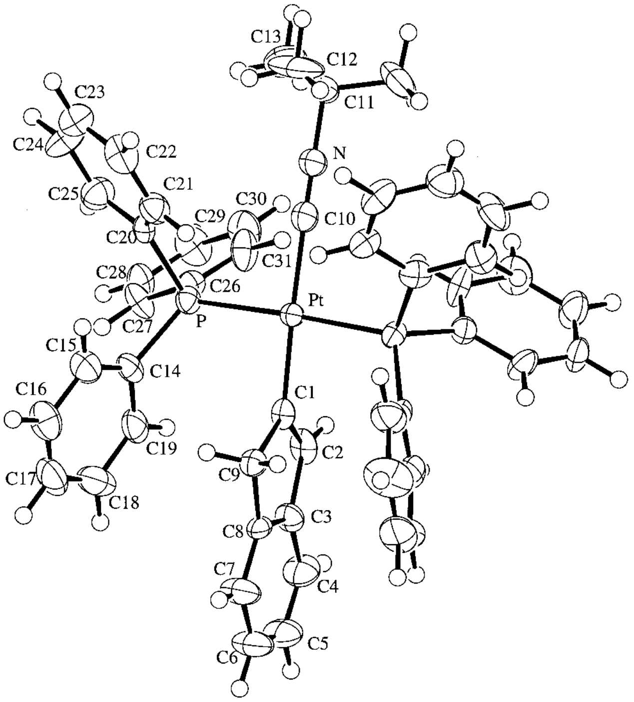


Figure 1. ORTEP drawing of the cationic complex in **4**·2THF. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn as circles with an artificial radius.

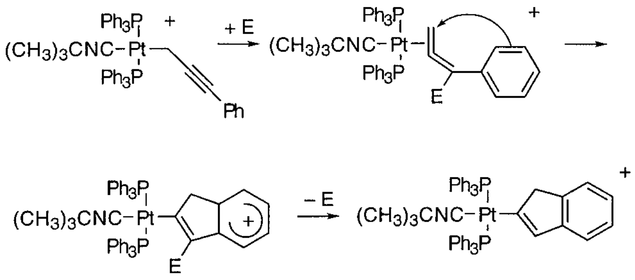
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4·2THF

Pt−P	2.328(2)	Pt−C(1)	2.037(15)
Pt−C(10)	1.999(17)	N−C(10)	1.11(2)
N−C(11)	1.50(2)	C(1)−C(2)	1.34(2)
C(1)−C(9)	1.49(2)	C(2)−C(3)	1.46(2)
C(3)−C(4)	1.41(2)	C(3)−C(8)	1.38(2)
C(4)−C(5)	1.37(2)	C(5)−C(6)	1.36(3)
C(6)−C(7)	1.41(3)	C(7)−C(8)	1.39(2)
C(8)−C(9)	1.48(2)	C(11)−C(12)	1.53(3)
C(11)−C(13)	1.50(2)		
P−Pt−P′[a]	177.1(2)	P−Pt−C(1)	88.80(7)
P−Pt−C(10)	91.28(7)	C(1)−Pt−C(10)	174.7(7)
C(10)−N−C(11)	179(2)	Pt−C(1)−C(2)	125(1)
Pt−C(1)−C(9)	126(1)	C(2)−C(1)−C(9)	108(1)
C(1)−C(2)−C(3)	111(2)	C(2)−C(3)−C(4)	132(2)
C(2)−C(3)−C(8)	107(2)	C(4)−C(3)−C(8)	121(2)
C(3)−C(4)−C(5)	119(2)	C(4)−C(5)−C(6)	120(2)
C(5)−C(6)−C(7)	121(2)	C(6)−C(7)−C(8)	119(2)
C(3)−C(8)−C(7)	119(2)	C(3)−C(8)−C(9)	109(2)
C(7)−C(8)−C(9)	132(2)	C(1)−C(9)−C(8)	104(1)
Pt−C(10)−N	177(2)	N−C(11)−C(12)	104(2)
N−C(11)−C(13)	106(1)		

[a] P′ is related to P by the crystallographic mirror plane $x, {}^1/_2 - y, z$.

reaction of η^1-propargyl complexes.[23] The involvement of a metal allene species would be consistent with the transient proton NMR resonance at 3.69 ppm (J_{PtH} = 20 Hz) observed for a possible intermediate in the rearrangement. This shift is close to that of 3.7 and 4.0 ppm found for two isomers of $CpRu(CO)_2(\eta^2\text{-}CH_2{=}C{=}CHPh)^+$.[24] If E is H^+ in our scheme, a signal for the CH proton also should be present. This resonance appears at 7.3 and 7.9 ppm in the Ru complexes, a region that is obscured because of the PPh_3 groups in our system. Also, the coupling between the CH and CH_2 protons (about 4 Hz in the Ru complexes), if present, cannot be resolved in the 3.69 ppm signal because of broadening due to unresolved coupling with phosphorus and the coupling to platinum. The failure of **2** to undergo rearrangement if the allenyl complex **3** is present would be explained if **3** reacts more rapidly with E than does **2** and thereby ties up the catalyst.

Scheme 1



Rearrangement of **2** to **4** requires the loss of an ortho proton from the phenyl ring on the propargyl group and addition of a proton to the five-membered ring, presumably at what becomes the CH position. Since no deuterium is incorporated into the indenyl group when the rearrangement occurs in CD_2Cl_2 or $CDCl_3$, these solvents cannot play a role in the rearrangement. Two other potential sources of this proton are the proton that is in the ortho position on the phenyl ring and any residual water in the solvent or on the glassware. Taken together, two different experiments confirm that water is the source of the proton.

That water can be the source of the proton was demonstrated by running the rearrangement reaction in CD_2Cl_2 in an NMR tube that was passified with D_2O prior to use and to which a drop of D_2O was added at the start of the reaction. The relative area of the CH signal of the five-membered ring of the resultant indenyl product was reduced to 46% of the expected value, while the area of the CH_2 group was unaffected. The presence of the CD group in some complexes of **4** was confirmed by ^2H NMR.

To test the ortho phenyl proton as a possible source of the CH proton in the indenyl complex, $[(PPh_3)_2Pt(\eta^1\text{-}CH_2CCC_6D_5)(CNC(CH_3)_3)]CF_3SO_3$ was synthesized, in which all of the phenyl protons on the propargyl group have been replaced with deuterium atoms. The indenyl complex resulting from the rearrangement of this compound showed no incorporation of deuterium at either the CH or CH_2 positions of the five-membered ring on the basis of relative areas of these two signals and by ^2H NMR. Hence, the proton that is lost from the carbon of the propargyl phenyl group does not get incorporated into the five-membered ring. Accordingly, if the rearrangement occurs as in Scheme 1, there must be proton exchange prior to formation of the CH bond of the five-membered indenyl ring. The mix of CH- and CD-containing indenyl product in the D_2O experiment must be due to incomplete removal of H_2O in the system.

When the initial reaction mixture of **1** and *tert*-butyl isocyanide is heated at 55 °C in the presence of a substantial excess of *tert*-butyl isocyanide, *trans*-$[(PPh_3)_2Pt(CN)(CNC(CH_3)_3)]CF_3SO_3$ (**5**) is obtained in high

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[23] Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Yaozeng, H., Eds.; Van Nostrand Reinhold: New York, 1982; pp 569−597.

[24] Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185.

yield. Neither **2** nor **3** remains as a product and must have reacted further to give **5**. This requires loss of the propargyl or allenyl group and may involve formation of *trans*-$[(PPh_3)_2Pt(CNC(CH_3)_3)_2](CF_3SO_3)_2$ as an intermediate product. The latter is observed to form in small amounts even at −30 °C when only a small excess of isocyanide is present (see Experimental Section). Dealkylation of one of the coordinated isocyanides of *trans*-$[(PPh_3)_2Pt(CNC(CH_3)_3)_2](CF_3SO_3)_2$ would lead to **5**. Isocyanides coordinated to both Pt(II)[25−27] and Pt(IV)[28] are well-known to undergo dealkylation.

In the interest of pursuing the generality of the above results, reaction 3 was carried out using $CNCH_2Ph$ in place of $CNC(CH_3)_3$. The reaction also was carried out using the analogous BF_4^- and PF_6^- salts of **1**. In all cases ^1H and ^{31}P NMR spectra confirmed the production of the comparable η^1-propargyl and -allenyl complexes in about the same proportion as in the reactions using $CNC(CH_3)_3$. However, separation of the pure propargyl complex could be achieved only in the BF_4^- and PF_6^- cases. This demonstrates the sensitivity of this separation to the nature of the coordinated isocyanide as well as to the counterion. Neither the BF_4^- nor the PF_6^- salt of the propargyl complex was observed to rearrange to an indenyl product in dichloromethane solution. On long storage in solution at room temperature, no changes occurred in the ^{31}P NMR spectrum. Heating a solution as in the case of **2** resulted in a gradual reduction over several days in the intensity of the propargyl complex peak in the ^{31}P NMR spectrum and the growth of the peak due to the allenyl complex, which eventually exceeded the propargyl complex in abundance. However, the intensity of the combined signals became weaker with time even as the allenyl-to-propargyl ratio continued to grow. The solution also became discolored, and other NMR signals began to appear. The equilibrium interconversion of η^1-propargyl and -allenyl platinum complexes has been studied for neutral complexes of the type *trans*-$Pt(CH_2C{\equiv}CPh)(X)(PPh_3)_2$ and is proposed to occur via an η^3-propargyl/allenyl intermediate.[29] The rate of interconversion depends on the identity of X. It seems likely that this mechanism also could be operative in our cationic isocyanide complexes and could account for the appearance of the allenyl complex. However, the slowness of the appearance of the allenyl complex and the accompanying decompositon suggest that equilibrium was not attained. The reason for the failure of the η^1-propargyl complexes containing $CNCH_2Ph$ to undergo rearrangement to an indenyl complex is not clear but may be due to the lower basicity of the $CNCH_2Ph$ group, which makes the propargyl group less susceptible to electrophilic attack (see Scheme 1).[23]

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Supporting Information Available: Tables of bond lengths and bond angles, atomic positional parameters, and anisotropic displacement parameters for **4**·2THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Treichel, P. M.; Hess, R. W. *J. Chem. Soc., Chem. Commun.* **1970**, 1626.

[26] Treichel, P. M.; Hess, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 4731.

[27] Treichel, P. M.; Knebel, W. J.; Hess, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5424.

[28] Crociani, B.; Nicolini, M.; Richards, R. L. *Inorg. Chim. Acta* **1975**, *12*, 35.

[29] Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *Inorg. Chim. Acta* **1997**, *265*, 9.