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Synthesis of Neutral Tetranuclear and Octanuclear Macrocyclic Platinum−Butadiyne Heterocyclynes

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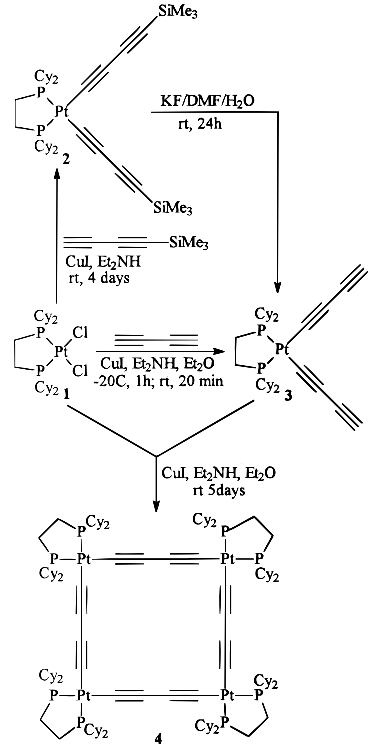
We have been studying the coordination chemistry of cyclic trialkyne ligands which we refer to as cyclynes and heterocyclynes. In these ligands the alkynes are arranged in a plane to produce a triangular cavity. In many instances a single metal atom can coordinate in the cavity to the three alkynes.[1] In the case of heterocyclynes, this coordination chemistry is somewhat reminiscent of that of acetylide tweezer complexes,[2] although the cyclic nature of the heterocyclyne ligand can give additional stabilization to the complex.[1j]

If the cavity of the heterocyclyne were larger, it could serve to coordinate multiatom species in the cavity. In regards to catenane and rotaxane[3] synthesis, interesting species to thread through a larger cavity include metal-acetylide polymers and carbon nanotubules. A larger cavity could be obtained by enlarging the ring to include more alkynes[4] and/or to include transition metals. Heterocyclynes with platinum atoms as the heteroatoms within the ring have been synthesized.[2q,5] Others have reported that charged[6] and neutral[7] macrocyclic tetrametallic planar squares can be assembled by strategies which involve knowledge of the coordination chemistry of the metal. These previously reported squares have edges composed of relatively bulky groups such as pyridine, 4,4′-bipyridine, 4,4′-dicyanobiphenyl, diazaperylene, and porphyrins. Herein we report the high-yield, gram-scale synthesis of tetraplatinum and octaplatinum square heterocyclynes which have large cavities and in which the rings are composed of only platinum and butadiyne fragments. These are the first reported examples of macrocycles where the ring is composed of only transition metals and alkynes. It should be noted that the relatively bulky groups on the edges of the previously reported platinum squares[6,7] increase the steric hindrance at the center relative to the squares reported here where the edges are composed of butadiynes. This makes their cavities more crowded and less likely to be good candidates for the formation of catenanes and rotaxanes threaded with metal−acetylide polymers and tubule derivatives.

Scheme 1. The Synthesis of the Platinum Butadiyne Heterocyclyne **4**



The synthesis of the square $[Pt(P_2C_2H_4(C_6H_{11})_4)C_4]_4$ **4** is outlined in Scheme 1. Chelating phosphines were used in order to enforce the required cis geometry at the platinum atom. The precursor 1,2-bis(dicyclohexylphosphino)ethane platinum dibutadiyne **3** was prepared by two different methods with both methods using the CuI-catalyzed[8] coupling of platinum with acetylides. Bubbling butadiyne[9] into a suspension of $[(C_6H_{11})_2P)_2C_2H_4]$-$PtCl_2$ **1**, diethylamine, diethyl ether, and a catalytic amount of

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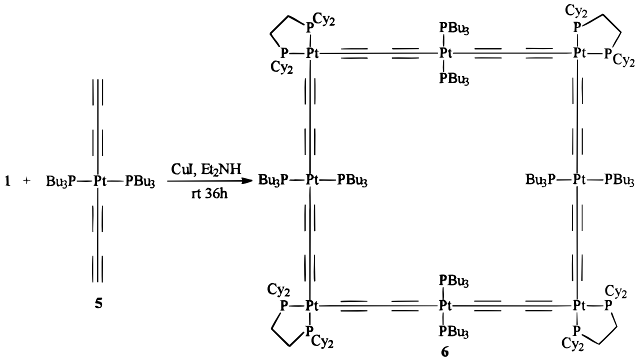
CuI at −20 °C for 1 h, followed by stirring at room temperature for 20 min gave **3** as a yellow powder in 95% yield. In the second method 1,2-bis(dicyclohexylphosphino)ethane platinum bis(trimethylsilylbutadiyne) **2** was synthesized by reacting $HC{\equiv}CC{\equiv}CSiMe_3$[9] with **1** in diethylamine in the presence of CuI at room temperature for 4 days. Workup and purification by flash chromatography on alumina eluting with 1:2 CH_2Cl_2/hexane gave **2** as a white solid. Reaction of **2** with KF and H_2O in DMF at room temperature for 24 h afforded **3** as a pale yellow powder in 65% yield. Compound **3** was characterized via ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR, IR, mass spectroscopy, elemental analysis, and X-ray crystallography.[10,11] A FAB-MS spectrum obtained from a methanol solution of **3** in a nitrobenzyl alcohol matrix showed M^+ of $^{12}C_{34}H_{50}P_2{}^{195}Pt$ at *m/z* 715.27 (calculated 715.30). Catalytic CuI coupling[8] of **1** with **3** in a mixture of 1:1 diethylamine/diethyl ether at room temperature for 5 days gave **4** in 98% yield (Scheme 1). Syntheses of **4** in large scale required longer reaction times for the reaction to go to completion. Compound **4** was characterized via ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{195}Pt NMR, IR, melting point, mass spectroscopy, and elemental analysis. A FAB-MS spectrum of a methanol solution of **4** in a nitrobenzyl alcohol matrix gave an M^+ of $^{12}C_{120}H_{192}{}^{195}Pt_4P_8$ at *m/z* 2661.05 (calculated 2661.15). The ^{195}Pt NMR for **4** showed a triplet at 1361 ppm ($J_{Pt-P} = 2287$ Hz). The $^{31}P\{^1H\}$NMR for **4** at 61.8 ppm ($J_{Pt-P} = 2293$ Hz) showed a shift upfield by nearly one ppm and a slight increase in the phosphorus−platinum coupling constant as compared to precursor **3** at 62.8 ppm ($J_{Pt-P} = 2285$ Hz). The $^{13}C\{^1H\}$ NMR ($CDCl_3$) showed a flip in the relative shifts of the α and β butadiyne carbons; in **3** the α carbons appeared at 99.9 ppm ($^2J_{\text{trans P-C}} = 135$ Hz, $^2J_{\text{cis P-C}} = 15$ Hz, $J_{Pt-C} = 1090$ Hz), and the β carbons at 93.3 ppm ($^3J_{\text{trans P-C}} = 32$ Hz, $^3J_{\text{cis P-C}} < 0.1$ Hz, $^2J_{Pt-C} = 308$ Hz), whereas in **4** the α carbons appeared at 94.7 ppm ($^2J_{\text{trans P-C}} = 139$ Hz, $^2J_{\text{cis P-C}} = 12$ Hz, $J_{Pt-C} = 1084$ Hz), and the β carbons at 98.9 ppm ($^3J_{\text{trans P-C}} = 32$ Hz, $^3J_{\text{cis P-C}} < 0.1$ Hz, $^2J_{Pt-C} = 313$ Hz), respectively. The α and β carbons in **3** and **4** were unambiguously assigned by their coupling constants to the phosphorus and platinum atoms. The IR spectrum of **3** exhibited two strong C≡C stretches at 2082 cm^{-1} (s) and 2146 cm^{-1} (s), and a ≡C−H stretch at 3307 cm^{-1}, whereas that of **4** showed C≡C stretches at 2075 cm^{-1} (w) and 2142 cm^{-1} (s). Under nitrogen, compound **3** decomposed at 165−168 °C, whereas **4** decomposed at 187−195 °C. Compound **4** is air stable in the solid state, but decomposes slowly in CH_2Cl_2, $CHCl_3$, C_6H_5Cl, and *o*-$C_6H_4Cl_2$ to form **1**. Compound **4** is soluble in the above halogenated solvents, DMSO, DMF, and MeOH and is slightly soluble in THF and acetone.

The octaplatinum heterocyclyne butadiyne square $[Pt(P_2C_2H_4(C_6H_{11})_4)C_4Pt(P(^nBu)_3)_2C_4]_4$ **6** was assembled from components which had the required cis and trans geometries at platinum, as shown in Scheme 2. The synthesis of bis(tri-*n*-butylphosphine) platinum dibutadiyne **5** was based on a method similar to that reported by Hagihara et al.[8,11a,12] Combining **1** with **5** in diethylamine in the presence of CuI at room temperature for 36 h gave **6** as a yellow powder in 80% yield. The ^{195}Pt NMR for **6** showed two triplets at 1369.4 ppm ($J_{Pt-P} = 2156$ Hz) and the other at 1529 ppm ($J_{Pt-P} = 2473$ Hz). The $^{31}P\{^1H\}$ NMR (C_6D_6) exhibits two sharp singlets with one at 5.7 ppm ($J_{Pt-P} = 2369$ Hz) and the other at 61.9 ppm ($J_{Pt-P} = 2242$ Hz). In $CDCl_3$ these peaks occur at 5.2 ppm ($J_{Pt-P} = 2403$ Hz) and 61.9 ppm ($J_{Pt-P} = 2261$ Hz). These are near the positions for the central peaks for **5** (5.5 ppm $J_{Pt-P} = 2288$ Hz) and **3** (62.8 ppm $J_{Pt-P} = 2285$ Hz) in $CDCl_3$ but shifted slightly and with a small difference in the P−Pt coupling constants. A FAB-MS spectrum obtained from a benzene solution of **6** in a nitrobenzyl alcohol matrix gave a broad molecular ion M^+ with a maximum at 5251.0 compared with a calculated value of 5250.49 for $^{12}C_{232}H_{408}{}^{195}Pt_8P_{16}$. Compound **6** is stable in nonhalogenated solvents. It is soluble in toluene, benzene, chloroform, methylene chloride, and acetone. Compound **6** reacts with chloroform to form a mixture of **1**, **3**, **5**, and bis(tri-*n*-butylphosphine)platinumdichloride within a few hours.

Scheme 2. The Synthesis of the Octaplatinum Butadiyne Heterocyclyne **6**



The combination of **4** with 1.5 equiv of AgOTf or $AgBF_4$ gave a mixture of products having **4** to Ag^+ ratios of 1:1 to 1:4 with the silver salts associated with the acetylide fragments of **4** in what we assume to be a tweezer[2] fashion. The principal product with AgOTf showed an absorption peak in the $^{31}P\{^1H\}$ NMR at 62.1 ppm ($J_{Pt-C} = 2423$ Hz) compared to **4** at 61.8 ppm ($J_{Pt-P} = 2293$ Hz) with several peaks a fraction of a ppm downfield from the major peak. The FAB mass spectrum gave a broad M^+ peak with a maximum at 3170.0 (cal 3172.77 for $^{12}C_{120}H_{192}{}^{195}Pt_4P_8({}^{108}AgSO_3CF_3)_2$. The MALDI mass spectrum gave a broad M^+ peak with a maximum at 2918 (cal 2916.96 for $^{12}C_{120}H_{192}{}^{195}Pt_4P_8{}^{108}AgSO_3CF_3$). Only one C≡C stretch (at 2102 cm^{-1}) was observed compared to two for **4** (see above). The FAB mass spectrum of the product of **4** with $AgBF_4$ gave a broad M^+ peak with maximum at 3434.4 which is consistent with compound **4** complexed with $4AgBF_4$ units with a calculated M^+ of 3436.78 ($^{12}C_{120}H_{192}{}^{195}Pt_4P_8({}^{108}AgBF_4)_4$). The MALDI mass spectrum gave a broad M^+ of 2772.49 (cal. 2768.06 for $^{12}C_{120}H_{192}{}^{195}Pt_4P_8{}^{108}Ag^+$).

We are currently synthesizing a variety of heterocyclyne alkyne squares of different sizes, and are examining the reaction chemistry of these carbon and platinum rich compounds. We are particularly interested in the threading of polyynes through **4** and the threading of nanotubules through **6**.

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Supporting Information Available: Experimental procedures and spectral data of products, tables of crystal data and structure refinement details, and bond distances and angles (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(10) Crystal data for $C_{34}H_{50}P_2Pt{\cdot}{}^1/_2CH_2Cl_2$: $M_r = 758.23$, monoclinic, space group *Cc*, $a = 20.707(7)$ Å, $b = 13.314(4)$ Å, $c = 13.038(4)$ Å, $\beta = 97.05(3)°$, $V = 3567(2)$ Å^3, $Z = 4$, $D_c = 1.412$ g cm^{-3}, $\mu = 4.118$ mm^{-1}, $F(000) = 1532$, $T = 178$ K. Difabs absorption correction. Refinement for data with $I > 2\sigma(I)$(2558 reflections) gave $R1(F) = 0.0511$ and $wR2(F^2) = 0.1130$ for all data.

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(12) Crystal data for $C_{32}H_{56}P_2Pt$: $M_r = 697.80$, triclinic, space group P^-1, $a = 9.6419(11)$ Å, $b = 9.9869(11)$ Å, $c = 18.376(2)$ Å, $\alpha = 102.120(9)°$, $\beta = 95.799(9)°$, $\gamma = 91.203(9)°$, $V = 1719.5(3)$ Å^3, $Z = 2$, $D_c = 1.348$ g cm^{-3}, $\mu = 4.190$ mm^{-1}, $F(000) = 712$, $T = 178$ K. Semiempirical absorption correction. Refinement for data with $I > 2\sigma(I)$(5428 reflections) gave $R1(F) = 0.0212$ and $wR2(F^2) = 0.0499$ for all data.