Figure 2. Experimental (left) and simulated (right) NMR spectra for *t*-Bu protons as a function of temperature for compound **1** in CD$_2$Cl$_2$; a and b mark the resonances of compounds **3** and **2**, respectively.

Pt^{III} complexes with either two (>0.10–0.15 Å) or four bridging ligands (>0.20–0.23 Å).[2,3,5–7]

The coordination sphere of Pt, including the intermetallic bond, is almost octahedral. The four equatorial sites are occupied by two cis chloride ions and two nitrogen atoms from the amide ligands; a third chloride ion occupies the apical position.

The Pt–Cl(eq) distances, 2.306 (3) and 2.328 (3) Å, are comparable to those found in K$_2$[PtCl$_4$] and K$_2$[PtCl$_6$] [2.316 (2)[11] and 2.323 (1) Å,[12] respectively]. The much longer Pt–Cl(ax) distance, 2.458 (3) Å, is indicative of a high *trans influence* exerted by the Pt^{III}–Pt^{III} bond. The corresponding distances were 2.407 (2) Å in K$_4$[Pt$_2$Cl$_2$(μ-P$_2$O$_5$H$_2$)$_4$],[4d] 2.448 (4) Å in (Et$_4$N)$_2$-[Pt$_2$Cl$_2$(μ-PO$_4$H$_2$)$_2$(μ-PO$_4$H)$_2$]·H$_2$O,[3e] and 2.444 (2) and 2.429 (4) Å in [Pt$_2$(μ-C$_5$H$_4$NO)$_2$Cl$_2$(NH$_3$)$_4$](NO$_3$)$_2$.[6d]

The Pt–N distances average 2.028 (10) Å, in the range of square-planar Pt^{II} and octahedral Pt^{IV} complexes.[6d,13]

The amide ligands are in the iminol tautomeric form, the hydrogens on the oxygen and on the nitrogen atoms having been located from the difference Fourier synthesis. The same tautomeric form was reported for *trans*-[PtCl$_2${HN=C(OH)C-(CH$_3$)$_3$}$_2$] and appears to be a common feature of platinum–amide complexes.[14] The C–N bond lengths [1.24 (1) and 1.26 (1) Å] and the coplanarity of H(N), N, Pt, and C(1) atoms also agree with an sp^2 hybridization of the N atoms. There are intramolecular hydrogen bonds between the apical chlorine ligand and one oxygen atom of a platinum subunit [Cl(1)···O(A) = 2.95 Å] and between the equatorial chlorine and the nitrogen atoms of twin subunits [N(A)···Cl(2′) = 3.18 Å and N(B)···Cl(3′) = 3.11 Å].

The complex adopts one of the two possible staggered conformations, placing the farthest away the amide ligands of the two platinum subunits; the values of the torsion angles about the Pt–Pt vector (ω) are close to 45°. This conformation was not allowed in platinum(III) dimers containing bridging ligands, for which the maximum value of ω was 26°.[1a,6c] The amide ligands are in equivalent pairs, and a 90° rotation of the two platinum subunits about the Pt–Pt vector interchanges the ligand positions

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and converts the complex into its enantiomeric form. Both enantiomers are found in the crystal.

The ^{1}H NMR spectrum shows two sets of signals of equal intensity for the amide ligands. Each set has resonances assignable to OH, NH, and C(CH$_3$)$_3$ protons, supporting the iminol bonding mode of all ligands. A line broadening was observed as a function of temperature, but the experiment had to be stopped well before coalescence because of the thermal lability of the compound (Figure 2). The fit to a unimolecular exchange process gave an approximate activation energy of 15.7 ± 0.5 kcal mol^{-1}. We suggest that complex **1** has in solution the same structure found in the solid and that the rotation about the Pt–Pt vector (which would lead to equivalence of the amide ligands by interchange of their positions) is slow on the NMR time scale. The barrier to rotation consists of the contribution of the steric repulsion between the two platinum subunits, which is built up in the eclipsed conformation, as well as the contribution of the intramolecular hydrogen bond disruptions.

The amide ligands appear to play a critical role in favoring the association of platinum units in oligomers. Considering this feature, the presence of amidate type bridging groups in several platinum oligomers, including the platinum blues,[15] appears not to be fortuitous.

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Asterane-like Compounds from 2,2,4,4-Tetramesityl-1,3-diphospha-2,4-disilabicyclo-[1.1.0]butane

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In an earlier report we described the reaction of tetramesityldisilene with white phosphorus in toluene at 40 °C to give the bicyclic title compound **1**.[1] Compound **1** behaved as a Lewis base toward transition metals, forming the tungsten carbonyl complexes **1**·W(CO)$_5$ and **1**·2[W(CO)$_5$]. In the previous communication the reaction of **1** with (Ph$_3$P)$_2$PtC$_2$H$_4$ was also described, leading to a compound (Mes$_2$Si)$_2$P$_2$Pt(PPh$_3$)$_2$, (**2**). At the time, it was not certain whether the product had the dative-bonded propellane structure **2b** or the tricyclo[1.1.1]pentane (asterane) structure **2a** in which the P–P bond is broken. An X-ray crystal structure determination has now shown that the asterane structure is

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Scheme I. Reactions of 1 Leading to Asterane Molecules
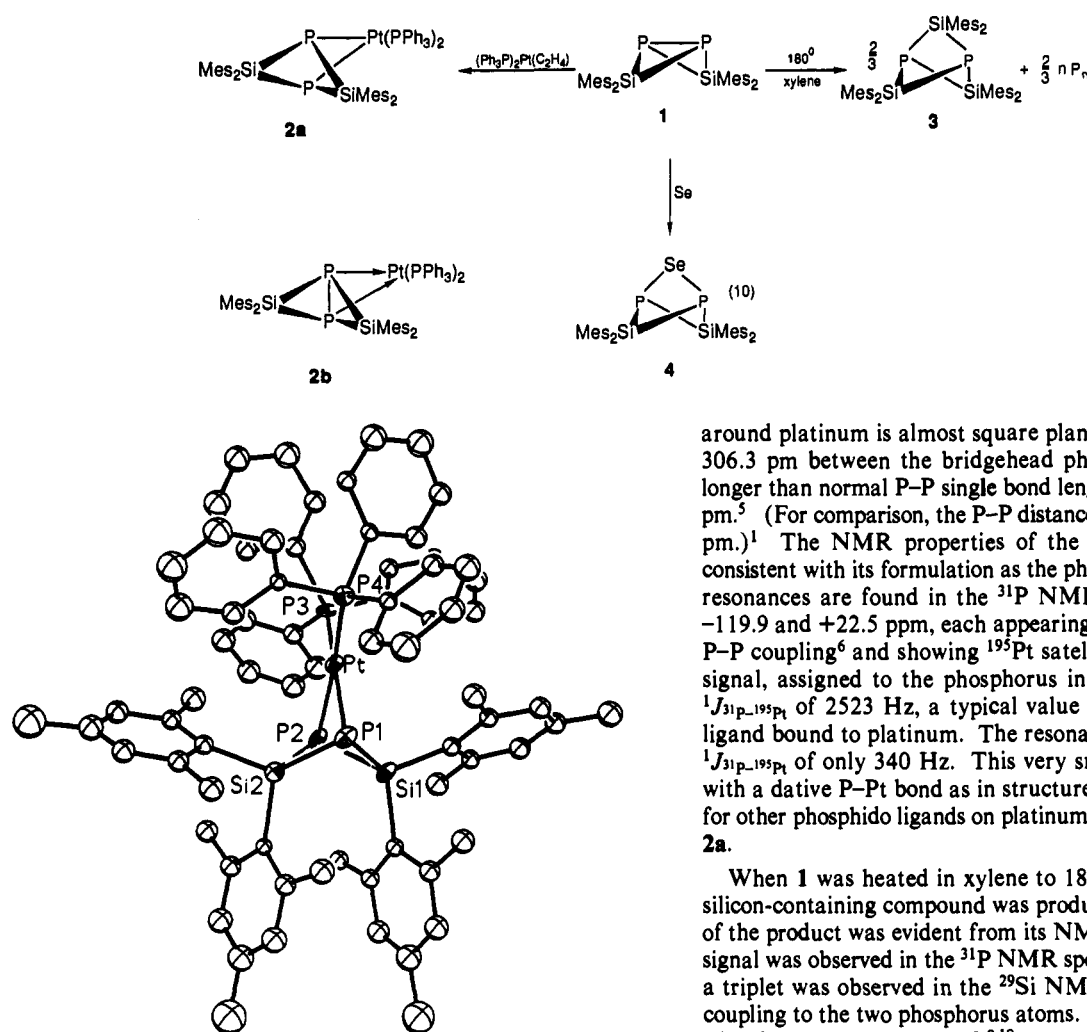
Figure 1. Thermal ellipsoid drawing for 2 (50% probability); hydrogens omitted for clarity. Bond lengths (pm): $P_1 \cdots P_2$, 306.3 (7); P_1–Si_1, 229.7 (7); P_1–Si_2, 227.4 (6); P_2–Si_1, 227.1 (5); P_2–Si_2, 230.6 (7); P_1–Pt, 242.7 (5); P_2–Pt, 241.9 (5); P_3–Pt, 234.9 (4); P_4–Pt, 234.8 (5). Bond angles (deg): P_1–Si–P_2, 84.3 (2); Si_1–P_1–Si_2, 79.4 (2), Si_1–P_2–Si_2, 79.3 (2); P_1–Pt–P_2, 78.4 (1); Si_1–P–Pt, 83.7 (2), 81.9 (2), 81.1 (2), 83.2 (2); P_3–Pt–P_4, 97.1 (2); P_1–Pt–P_3, 168.9 (2); P_1–Pt–P_4, 170.3 (2).

correct.[2,3] Furthermore, the thermolysis of 1 at 180 °C and the reaction of 1 with selenium also lead to asterane-like structures, 3 and 4, as shown in Scheme I.

A thermal ellipsoid drawing of 2 is shown in Figure 1, along with important bond lengths and angles.[4] The arrangement

around platinum is almost square planar. The $P \cdots P$ distance of 306.3 pm between the bridgehead phosphorus atoms is much longer than normal P–P single bond lengths, which are about 222 pm.[5] (For comparison, the P–P distance in 1·2[W(CO)₅] is 234.2 pm.)[1] The NMR properties of the platinum compound are consistent with its formulation as the phosphido complex 2a. Two resonances are found in the ^{31}P NMR spectrum of 2a at δ = −119.9 and +22.5 ppm, each appearing as a pseudotriplet due to P–P coupling[6] and showing ^{195}Pt satellite lines. The downfield signal, assigned to the phosphorus in the PPh₃ groups, had a $^1J_{31P\_195Pt}$ of 2523 Hz, a typical value for a triphenylphosphine ligand bound to platinum. The resonance at −119.9 ppm had a $^1J_{31P\_195Pt}$ of only 340 Hz. This very small value is inconsistent with a dative P–Pt bond as in structure 2b, but is similar to that for other phosphido ligands on platinum,[7] and so is consistent with 2a.

When 1 was heated in xylene to 180 °C for 5 days, a single silicon-containing compound was produced. The high symmetry of the product was evident from its NMR spectra. Only a single signal was observed in the ^{31}P NMR spectrum (δ = 41 ppm), and a triplet was observed in the ^{29}Si NMR spectrum due to equal coupling to the two phosphorus atoms. These data are consistent with the asterane structure 3.[9,10] A preliminary crystal structure, as yet unrefined, confirms this formulation.

When a solution of 1 was stirred with elemental selenium[11] at 30 °C for 20 days, a new compound was produced, which appears to have structure 4.[12] This product shows a singlet in the ^{31}P

(2) Experimental procedure for 2: A solution of 1 (200 mg, 0.34 mmol) in 10 mL of toluene was treated with solid Pt(PPh₃)₂(C₂H₄) (242 mg, 0.34 mmol) at 0 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature and stirred for an additional 2 h. The toluene was removed in vacuo, and the residue was recrystallized from benzene to yield 331 mg (74%) of 2 as a yellow-orange solid: mp = 188–194 °C dec; ^{1}H NMR (C₆D₆/C₇D₈) δ 2.118 (s, 6 H), 2.332 (s, 6 H), 2.761 (s, 12 H), 2.767 (s, 12 H), 6.406 (s, 4 H), 6.842 (s, 4 H), 6.9 (m, 20 H), 7.1 (m, 10 H); ^{29}Si NMR (INEPT, C₆D₆/C₇D₈) δ −27.0 (t, $|^1J_{Si\_P}|$ = 65 Hz); ^{31}P NMR (C₆D₆/C₇D₈) δ −119.9 (pseudo-t, SiPPt, $|^2J_{P\_PPh_3}$(cis) + $^2J_{PPh_3}$(trans)| = 28 Hz, $|^1J_{P\_P}|$ = 340 Hz), +22.5 (pseudo-t, PtPPh₃, $|^1J_{P\_P}|$ = 2523 Hz); MS (FAB, 3-NO₂-(C₆H₄)CH₂OH matrix) m/z 1346 (10, [M + matrix fragment]⁺).

(3) For related examples of oxidative addition of strained P–P bonds to platinum, see: Phillips, I. G.; Cavell, R. G. *Phosphorus Sulfur* 1987, 30, 117. Phillips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* 1988, 27, 2269.

(4) Crystal structure analysis of 2: C₇₂H₇₄P₄Si₂Pt·3.6(C₆H₆), yellow prisms from benzene; crystal dimensions 0.10 × 0.20 × 0.25 mm, triclinic, space group P1, a = 13.753 (7) Å, b = 14.092 (5) Å, c = 23.160 (9) Å, α = 72.00 (3)°, β = 81.83 (4)°, γ = 87.19 (4)°, V = 4226 (3) Å³, Z = 2, F_w = 1595.7, ρ_{calcd} = 1.254 g cm⁻¹, μ = 1.821 mm⁻¹ (Mo Kα), T = 153 K; 4401 independent data (2θ_max = 45°), 4024 observed data $|F| > 3\sigma(F)$, structure solution by Patterson methods; R = 0.058, R_w = 0.0739 using $w^{-1} = \sigma^2(F) + 0.0003F^2$.

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(6) The ^{31}P NMR spectrum for compound 2a is actually an AA'XX' system, with $J_{AA'}$ and $J_{XX'}$ so small that the peaks appear as virtual triplets. The low value of $|^2J_{PP}$(cis) + $^2J_{PP}$(trans)|, 28 Hz, confirms that 2a is a phosphido complex. The $^2J_{PP}$(trans) values in square-planar phoshine–Pt complexes are normally several hundred hertz,[7] but phosphido–Pt complexes show very small $^2J_{PP}$ values.[8]

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(8) Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Dalton Trans.* 1984, 2237.

(9) Experimental procedure for 3: A sealed tube containing 1 (150 mg, 0.25 mmol) in 3 mL of xylene was heated to 180 °C for 4 days. The reaction mixture was then filtered and recrystallized from cold hexane to give 6 as a colorless solid: yield 103 mg (72%); ^{1}H NMR (C₆H₆) δ 2.03 (s, 18 H), 2.66 (s, 18 H), 2.69 (s, 18 H), 6.16 (s, 6 H), 6.49 (s, 6 H); ^{29}Si NMR (INEPT, C₆D₆) δ −27.12 (t, $|^1J_{Si\_P}|$ = 41 Hz); ^{31}P NMR (C₆D₆) δ 40.73 (s, $|^1J_{Si\_P}|$ = 41 Hz); MS (FAB, 3-NO₂(C₆H₄)CH₂OH matrix) m/z 860.

(10) A compound with a structure similar to that of 3 but with methyl groups on Si has been described earlier: Fritz, G.; Amann, P. *Z. Anorg. Allg. Chem.* 1986, 535, 95. The methyl compound was reported to rearrange at 120 °C to an adamantane structure. Compound 3 does not undergo such a rearrangement, but instead decomposes above 270 °C into more complex products.

(11) For a previously reported insertion of Se into a P–P bond, see: duMont, W. W.; Hensel, R.; McFarlane, W.; Colquhoun, I. J.; Ziegler, M. L.; Serhadli, O. *Chem. Ber.* 1989, 122, 37.

NMR spectrum at +146 ppm, with ^{29}Si and ^{77}Se satellites, and triplets in the ^{29}Si and ^{77}Se NMR spectra. The observed $^1J_{31P-77Se}$ value of 83 Hz seems to be one of the lowest ever recorded. Normal P–Se bonds in acyclic molecules show ^1J values of –200 to –400 Hz,[13] but smaller values, –100 to –270 Hz, have been observed for phosphorus–selenium rings and cages.[14]

The examples of **2a**, **3**, and **4** indicate that reactions of **1** that break the P–P bond and lead to asterane-like molecules may be fairly general. Additional examples of such structures can be expected in the future.

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Supplementary Material Available: Structure determination summary, Table I containing atomic coordinates, equivalent isotropic displacement factors, and occupanices, Table II containing bond lengths, Table III containing bond angles, and a thermal ellipsoid drawing for **2** (11 pages). Ordering information is given on any current masthead page.

(12) Experimental procedure for **4**: To a solution of **1** (150 mg, 0.25 mmol) and 5 mL of hexane was added Se metal (100 mg, 1.25 mmol, 5 equiv). The solution was stirred for 10 days at 30 °C. The reaction mixture was filtered and recrystallized from hexane at –78 °C to give **4** as a yellow solid, which was 80% pure by ^{31}P NMR (20% was **1** that could not be removed): yield 89 mg (53%); ^1H NMR (C_6D_6) δ 1.99 (s, 6 H), 2.13 (s, 6 H), 2.33 (s, 12 H), 2.95 (s, 12 H), 6.30 (s, 4 H), 6.80 (s, 4 H); ^{29}Si NMR (INEPT, C_6D_6) δ –11.25 (t, $|^1J_{SiP}|$ = 29 Hz); ^{31}P NMR (C_6D_6) δ +146.66 (s, $|^1J_{Si-P}|$ = 29 Hz, $|^1J_{Se-P}|$ = 83 Hz); ^{77}Se NMR (C_6D_6) δ 64.2 (t, $|^1J_{Se-P}|$ = 83 Hz); MS (FD, 3 mA) m/z 672, 674 (^{78}Se, ^{80}Se), (EI) m/z [M – P]$^+$ calcd 641.1892, found 641.1891.

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Cyclopropylcarbene–Tungsten Complexes + Alkynes: A [4 + 2 + 1] Cycloaddition Route for the Construction of Seven-Membered Rings

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Carbocyclic seven-membered rings are present in a variety of medicinally important compounds and are typically constructed by ring expansion reactions, cyclization reactions, reactions of other seven-membered rings, and occasionally cycloaddition reactions. Cycloaddition reactions have the greatest potential, but few leading to direct formation of a seven-membered ring have been reported.[1] To develop a seven membered ring forming cycloaddition reaction, the reaction between cyclopropylcarbene–chromium complexes and alkynes was examined (Scheme I). This reaction produced
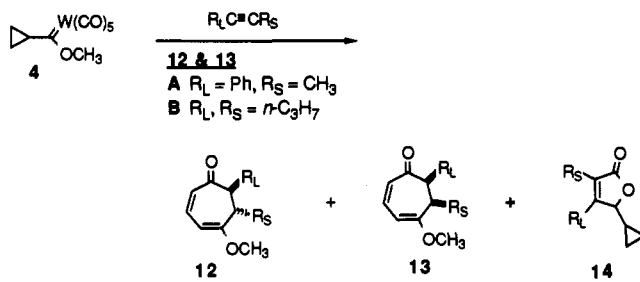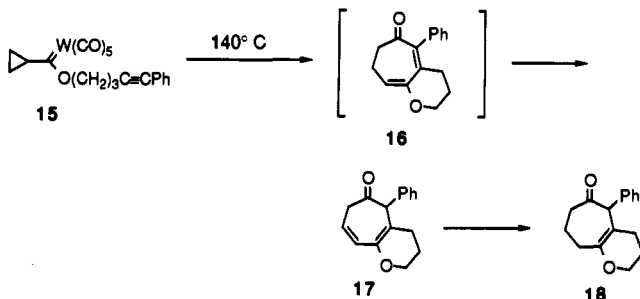
Scheme I
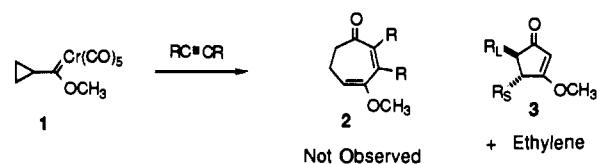
Scheme II

Scheme III

A R_L = Ph, R_S = CH$_3$
B R_L, R_S = n-C$_3$H$_7$
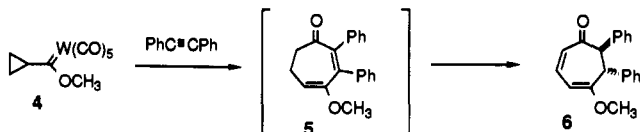
Scheme IV

not cycloheptadienone **2**, but cyclopentenone **3** plus ethylene.[2] Herein we report initial studies of the reaction of the tungsten analogue of **1** (complex **4**) with alkynes, which leads to the desired cycloheptadienones.[3]

First, the reaction between diphenylacetylene and tungsten carbene complex **4** was examined. At 100 °C in dioxane, cycloheptadienone derivative **5** was produced in 21% yield along with a trace of rearranged cycloheptadienone **6** (Scheme II). Longer reflux times led to formation of greater amounts of cycloheptadienone **6** at the expense of **5**. Cycloheptadienone **5** was converted to **6** after 2 h at 140 °C; the mechanism presumably involves consecutive 1,5-hydride shifts.[4] In contrast to previous results obtained with alkylcarbene–tungsten complexes and alkynes,[5] the cycloaddition reaction was never complete at 100 °C. Optimal yields of cycloheptadienone **6** (55%) were obtained when the reaction was conducted in refluxing xylene (140 °C) in the presence of 1,2-bis(diphenylphosphino)benzene. Cycloadduct

(1) Some examples of seven-membered ring-forming cycloaddition reactions include the following: (a) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* 1989, *54*, 930–936. (b) Noyori, R. *Acc. Chem. Res.* 1979, *12*, 61–66. (c) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 1–19. (d) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* 1988, *110*, 2653–2655. (e) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* 1987, *109*, 3483–3484. (f) Molander, G. A.; Cameron, K. A. *J. Org. Chem.* 1991, *56*, 2617–2619. (g) Boger, D. L.; Brotherton, C. E. *J. Org. Chem.* 1985, *50*, 3425–3427. (h) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* 1991, *113*, 5066–5068. (i) Wender, P. A.; Lee, H. Y.; Wilhelm, R. S.; Williams, P. D. *J. Am. Chem. Soc.* 1989, *111*, 8954–8957.

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