ORGANOMETALLICS

Subscriber access provided by CUNY CENTRAL OFFICE

Platinacyclobutane chemistry: cis-disubstituted platinacyclobutane complex from bicyclo[4.1.0]heptane

E. J. Parsons, and P. W. Jennings

Organometallics, **1988**, 7 (6), 1435-1437• DOI: 10.1021/om00096a032 • Publication Date (Web): 01 May 2002

Downloaded from http://pubs.acs.org on April 28, 2009

More About This Article

The permalink http://dx.doi.org/10.1021/om00096a032 provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

ACS Publications
High quality. High impact.

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Platinacyclobutane Chemistry: Cis-Disubstituted Platinacyclobutane Complex from Bicyclo[4.1.0]heptane

E. J. Parsons and P. W. Jennings*

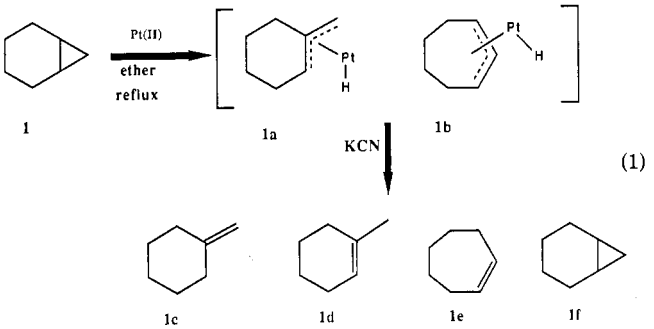
Gaines Hall, Montana State University, Bozeman, Montana 59717

Received January 27, 1988

The methodology for the preparation, isolation, and characterization of platinacyclobutanes from cis-disubstituted cyclopropane derivatives is established. In this case the metallacyclobutane was successfully prepared and characterized from bicyclo[4.1.0]heptane. Further, it is now quite reasonable to suggest that this platinacyclobutane complex is an intermediate in the reaction of Zeise's dimer, Pt(II), with bicyclo-[4.1.0]heptane. Finally, the concept that π-allyl complexes are the only result of reacting Pt(II) with cis-disubstituted cyclopropane derivatives has been refuted.

Introduction

Early work by Brown[1] and McQuillin[2] suggested that π-allyl complexes were intermediates in the reaction of Pt(II) with cis-disubstituted cyclopropanes (eq 1). Com-



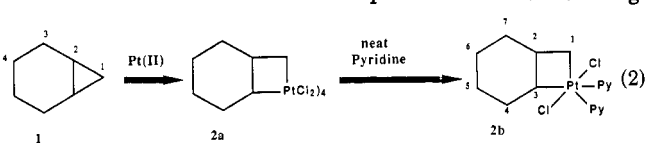
1 1a 1b 1c 1d 1e 1f (1)

plexes **1a** and **1b** were neither isolated nor characterized but were inferred as intermediates leading to **1c–f**. Unfortunately, this led subsequent investigators to conclude the platinacyclobutane complexes could not be prepared or isolated from cis-disubstituted cyclopropanes.[3]

Results from our laboratory, reported in 1982, clearly refuted the above results for the cases in which the cyclopropyl moiety was part of a norbornyl system.[4] Since these complexes were readily prepared and quite stable, an effort was subsequently supported to prepare, characterize, and explore the chemistry of platinacycles from compounds such as 1. In this paper, we report the successful formation of the platinacyclobutane of 1 and reactions of this complex under conditions analogous to those reported to give π-allyl intermediates.[2]

Results and Discussion

Preparation and Characterization of Platinacyclobutanes from 1. Complexes **2a** and **2b**, shown in eq 2, are not as readily prepared nor are they as stable as those from the norbornyl or bicyclo[6.1.0]nonane systems.[4,5] The best method at the present time for forming



1 2a 2b (2)

2a is to allow 1 to react with Pt(II) [Zeise's dimer] at −10 °C over a 36-h period (32% yield).[6] It is important to mention that **2a** will decompose on standing at room temperature. Attempted formation of **2b** by reacting **2a** with 2 equiv of pyridine leads to immediate decomposition. However, solvation in neat pyridine yields **2b** readily and provides a very stable platinacyclobutane in solution.

The key NMR data for complex **2b** are typical[4,5] of other known platinacyclobutane: ^{195}Pt, 3315 pm (relative to $Na_2Pt(CN)_4$ in D_2O); ^{13}C, −8.6 (C(1), t, $J_{Pt,C}$ = 354 Hz), 44.6 d, (C(2), $J_{Pt,C}$ = 98), 5.8 ppm (C(3), d, $J_{Pt,C}$ = 369 Hz). Since the pyridine derivative could not be readily isolated, a stable bipyridine derivative was prepared and isolated. Its key NMR characteristics were nearly identical with those observed for the pyridine derivative [^{195}Pt, 3095 ppm; ^{13}C, −7.7 (C(1), t, $J_{Pt,C}$ = 342 Hz), 42.8 (C(2), d, $J_{Pt,C}$ = 92 Hz), and 5.2 ppm (C(3), d, $J_{Pt,C}$ = 366 Hz)]. Thus, it is now clear that cis-disubstituted platinacyclobutane complexes may be prepared from a variety of cis-disubstituted cyclopropane systems.[4,5]

Reactions of Complex 2a. Complex **2a** exhibited typical platinacyclobutane behavior toward aqueous KCN and Ph_3P by reductively eliminating compound 1. It is important to note the reaction with KCN as it becomes significant in subsequent arguments.

The major goal of this investigation, however, was to determine if the results reported earlier by McQuillin could be accommodated by a platinacyclobutane rather than a π-allyl intermediate. Thus, it is important to reiterate the conditions of his experiment: Compound 1 was refluxed in ether for 1 h with Zeise's dimer (Pt(II)) which formed an orange precipitate. Subsequent treatment with aqueous KCN gave **1c–f** in a ratio of 2:2:1:?, respectively, by GC analysis. Compound **1f** was observed, but its concentration relative to the others was not stated.

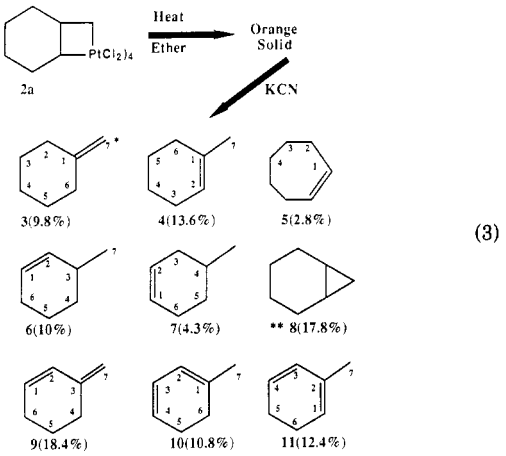
In our laboratory, under the same conditions, complex **2a** yields the products shown in eq 3. Clearly this mixture is more complex than that shown in eq 1 and apparently is not in concert with the earlier results of McQuillin. However, repetition of McQuillin's experiment as stated above with 1 gave the same mixture as was obtained from **2a** (Figure 1).

With the exception of diolefin **11**, each of the compounds **3–11** was identified by comparison with authentic samples using NMR and GC–mass spectroscopy (see Experimental Section for detailed data and syntheses of select compounds). Relative yields were garnered from capilllary GC using the total ion current unit of a mass spectrometer as the detector. Compound 11 was not synthesized but was

(1) Cushman, B. M.; Earnest, S. E.; Brown, D. B. *J. Organomet. Chem.* **1978**, *159*, 431.
(2) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.
(3) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.
(4) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385, 1370.
(5) Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109* 3973.

(6) It is important to note that an error was made in the Experimental Section of the paper cited as ref 5. For preparing the platinacycle of the bicyclo[6.1.0]nonane, it is necessary to stir the hydrocarbon and Pt(II) for 36 h and then rapidly evaporate the solvent to dryness at 0 °C.

0276-7333/88/2307-1435$01.50/0 © 1988 American Chemical Society



(3)

identified by comparison of its ^{1}H NMR spectrum and GC–MS fragmentation pattern to that reported in the literature.[7] Further evidence for both **10** and **11** was obtained by showing that they formed Diels–Alder products by reaction of the total mixture with maleic anhydride.

The origin of every component in the reaction mixture was not specifically determined. However, it is clear that products **5** and **8** are among the primary compounds formed. For instance, treatment of **5** with Zeise's dimer for 1 h (reaction conditions) gave only cycloheptene as ascertained by GC mass spectroscopy using the capillary column. Product **8** is derived from the cyanide facilitated reductive elimination of unreacted **2a**. This is evidenced both by the fact that **2a** yields **8** on treatment with aqueous KCN (vida supra) and the fact that <1% of **8** is present in the reaction mixture prior to reaction with KCN. This was determined by ^{1}H NMR and mass spectroscopy on the reaction mixture of eq 3. Reaction of **3** or **4** under reaction conditions yields a mixture of **3**–**11** save **5** and **8**.

Finally, it is imporant to note in Figure 1 that compound **3** eluted near **6** and **7** and that **4** is in a group with **10** and **11**, **5** is with **9**, and **8** is by itself (i.e. four groups of peaks). Thus, a reasonable scenario is that McQuillin's GC column did not have adequate resolving capacity to separate all of the isomers. Hence, he observed only four peaks which, when subjected to standard addition techniques, would lead to the conclusion that compounds **3**, **4**, **5**, and **8** were the reaction products.

It now appears reasonable to conclude that compound **1** reacts with Zeise's dimer to form platinacyclobutane **2a** which subsequently decomposes thermally to yield a plethora of olefinic products. It is tempting to suggest that McQuillin was actually correct in that π-allyl complexes are responsible for the products and that we are simply adding that a platinacyclobutane complex is a precursor to the π-allyl intermediate. However, we recently[5] demonstrated, as Puddephatt[9] had earlier, that other complexes analogous to compound **3** may be formed by an initial α-hydride transfer mechanism that does not require a π-allyl intermediate. Subsequent studies may also prove that alternative pathways are functioning in the formation of the other products. Thus, it appears premature to rigorously conclude that π-allyl intermediates are required for the reactions shown in eq 1 and 3.

(7) Ruttiman, A.; Wick, A.; Eschenmoser, A. *Helv. Chim. Acta.* **1975**, *58*, 1450.
(8) Puddephatt, R. J.; Al-Essa, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 45. Puddephatt, R. J.; Ling, S. S. M. *J. Chem. Soc., Chem. Commun.* **1982**, 412.
(9) Littlecott, G. W.; McQuillin, F. J.; Powell, K. G. *Inorg. Synth.* **1976**, *16*, 113.

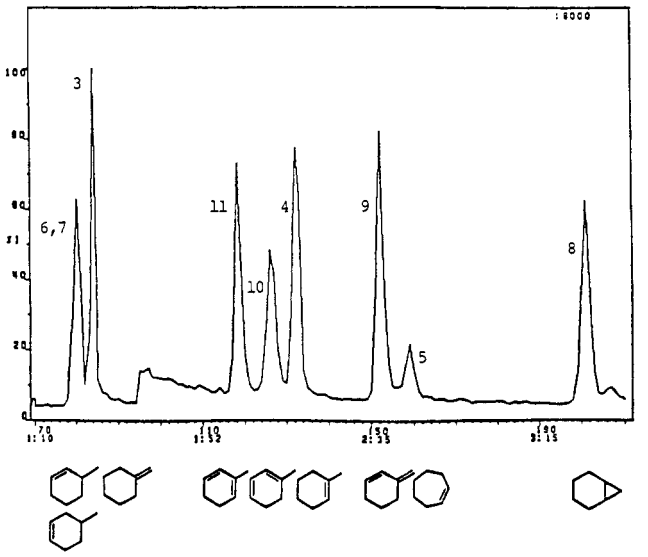


Figure 1. GC trace of the products of reactions 1 and 3 as monitored by the total ion current detector.

Table I. NMR Resonances for Compounds 2b (L = py or $^1/_2$ bpy)

C or H no.	L (solv) py (py)	$^1/_2$bpy ($CDCl_3$)
	^{13}C NMR[d]	
1	−8.6 t (354)[b]	−7.7 t (342)
2	44.6 d (98)	42.8 d (92)
3	5.8 d (369)	5.2 d (366)
4[a]	27.2 t	27.5 t (24)
5[a]	20.4 t	20.3 t (43)
6[a]	19.9 t	19.4 t (49)
7[a]	25.7 t	24.7 t (15)
	^{1}H NMR[d]	
1a	3.0 d	2.7 dd (85)
1b	2.8 dd	2.4 dd (80)
2	3.0 m	3.1 m
3	3.7 ddd (93)	3.3 ddd (92)
4a	2.2 m	2.0 m
4b–7a	1.5 m	1.6 m
7b	2.0 m	1.6 m
	^{195}Pt NMR[d]	
	3315[c]	3095

[a] Not rigorously assigned. [b] Platinum coupling in Hz. [c] Relative to 1.0M $Na_2Pt(CN)_4$ in D_2O at 25 °C. [d] All shifts in ppm.

Summary. The postulate that platinacyclobutane complexes cannot be prepared from *cis*-1,2-dialkyl-substituted cyclopropanes is incorrect. A number of norbornyl systems and now two bicyclo[*X*.1.0]hydrocarbons have been reacted with Pt(II) to successfully form platinacyclobutane complexes.[5] However, it is important to note that the bicyclo[*X*.1.0] systems are less thermally stable than the norbornyl systems. Their reductive elimination chemistry is characteristic of platinacyclobutanes in reactions with CN^- and Ph_3P. Finally, thermal degradation of the platinacyclobutane in ether leads to the same product distribution as is observed by heating the bicyclo[4.1.0]heptane with Pt(II). Thus, it appears reasonable to postulate that a platinacyclobutane complex is an intermediate in the platinum-facilitated rearrangement of bicyclo[4.1.0]heptane.

Experimental Section

General Data. NMR spectra were obtained on a Bruker WM250 spectrometer, and mass spectral data were acquired by using VG-16 and 7070 spectrometers. The capillary GC column

Table II. ^1H, ^{13}C NMR, and MS Data for Compounds 1, 3–7, and 9–11

	1	3		4		5		6						10	11	
H or C no.		H no.		H no.		H no.		H no.		H no.	7	9		obsd	obsd	ref 18
								^1H NMR[b]								
1a	−0.03 dd	1	...	1	...	1	5.77 dd	1	5.63 ddd	1	5.64 d	5.82 ddd	...		5.46 dd[a]	5.45 m
1b	0.50 m	2	2.10 b s[a]	2	5.36 dd	2	2.10 m	2	5.50 dd	2	5.64 d	6.13 ddd	5.63 m		...	
2	0.82 m	3	1.51 b s[a]	3	1.91 m[a]	3	1.49 m	3	2.15 m	23	1.63 m[a]	...	5.83 m		5.79 m[a]	5.78 m
3a	1.55 m[a]	4	1.51 b s[a]	4	1.56 m[a]	4	1.70 m	4	1.50 m[a]	4	1.19 m[a]	2.10 bdd	5.63 m		5.46 m[a]	5.45 m
3b	1.85 m[a]	5	1.51 b s[a]	5	1.56 m[a]			4	1.15 m[a]	5	1.63 m[a]	1.70 ddd	2.14 m		2.1 m[a]	2.08 m
4a	1.18 m[a]	6	2.10 b s[a]	6	1.91 m[a]			5	1.73 m[a]	6	2.03 m[a]	2.33 ddd	2.07 b d		2.1 m[a]	2.08 m
4b	1.18 m[a]	7	4.55 s	7	1.61 b s			6	1.94 m[a]	7	0.94 d	4.73 2b s	1.76 b s		1.7 b s	1.7 b s
								7	0.94 d							
								^{13}C NMR[b]								
1	10.0 t					132.3 d										
2	9.2 d					29.4 t[a]										
3	23.8 t[a]					27.7 t[a]										
4	21.3 t[a]					32.6 t										
								MS[c]								
	96 (46.9)	96 (46.6)		96 (35.4)		96 (53.4)		96 (24.4)		96 (34.1)	94 (34.0)	94 (41.8)		94 (37.8)	94 (42)	
	81 (71.7)	81 (100)		81 (100)		81 (71.2)		81 (100)		81 (100)	93 (12.3)	93 (16.6)		93 (14.5)	93 (16)	
	67 (100)	67 (81.5)		81 (42.4)		67 (100)		81 (38.2)		67 (32.5)	91 (16.2)	92 (31.1)		91 (28.0)	91 (30)	
	54 (79.5)	55 (43.5)		55 (29.7)		54 (91.6)		54 (33.0)		55 (69.2)	79 (100)	91 (58.2)		79 (100)	79 (100)	
	42 (35.9)	42 (28.0)		42 (18.2)		42 (33.7)		42 (25.9)		42 (22.2)	77 (33.7)	79 (100)		77 (44.9)	77 (49)	
											66 (14.5)	77 (45.0)		65 (12.1)		
											65 (10.8)	65 (14.1)		48 (14.7)		
											53 (12.7)	51 (13.9)				
											51 (10.4)					

[a] Not rigorously determined. [b] Shifts in ppm; $CDCl_3$ solvent. [c] m/e (relative intensity).

was 30 m × 0.25 mm. i.d. coated to 250 μm with DB-5 from J and W Scientific.

Chemicals. Pyridine-d_5 and $CDCl_3$ were obtained from Stohler/KOR Stable Isotopes and Norell Inc. Diethyl ether was distilled from CaH_2 prior to use, and diazomethane was generated from Aldrich Diazald. Zeise's dimer was prepared from K_2PtCl_4 by the published procedure.[9]

Hydrocarbons. Compound **1** was prepared from cyclohexene by using the procedure published by Rawson and Harrison.[10] ^1H, ^{13}C, and MS spectral data were in agreement with those published in ref 11, 12, and 13, respectively. Compounds **3**, **4**, **5**, **6**, and **7** were purchased from Aldrich and were distilled prior to use. Compound **9** was prepared by the method of Wittig and Schoellkopf.[14] Compound **10** was obtained by the method published by Birch and Subba Rao.[15] (^1H and MS data are in ref. 16 and 17).

Preparation of Platinacycles 2a and 2b. To a cooled (−10 °C) solution containing **1** (0.033 g, 0.34 mol) in 2 mL of dry ether, was added 0.05 g (0.17 mol) of Zeise's dimer. The suspension was maintained at −10 °C with stirring for 36 h and then rapidly evaporated to dryness at 0 °C. Due to its thermal instability, **2a** was immediately reacted with neat pyridine to form **2b** which appears to be infinitely stable in solution. The complete NMR data for **2b** (L = pyridine and L = $^1/_2$bipyridine) are listed in Table I. The bipyridine adduct was prepared by the addition of 4 equivs of 2,2′-bipyridine to the pyridine solution of **2b**. Subsequent rotoevaporation gave a yellow or pink solid which, when chromatographed on silica with chloroform as the eluting solvent, gave the pale yellow solid **2b** (L = $^1/_2$bipyridine) in 87% yield. Analytical data for the bipyridine complex are listed below. Calcd for $C_{17}H_{20}N_2Cl_2Pt$: C, 39.39; H, 3.89. Found: C, 38.80; H, 3.84.

Thermal Decompositon of 2a in Ether. Complex **2a** (0.02 g, 0.06 mol) was prepared and isolated as discussed above and was immediately refluxed in ether for 1 h. The ether was removed under vacuum to yield a solid product that dissolved rapidly when treated with aqueous KCN (0.21 g, 0.32 mmol). Extraction with chloroform and analysis via ^1H NMR and mass spectroscopy revealed the presence of compounds **3**–**11**. This analysis relied on the use of standards for comparative confirmations with both NMR and MS. Compound **11** was identified by comparison of its ^1H NMR and particularly its mass spectral fragmentation pattern with those reported in the literature.[18] Listed below are the ^1H and ^{13}C NMR and MS fragmentation pattern for compounds **1**, **3**, **4**, **5**, **6**, **7**, **9**, **10**, and **11**.

Reaction of 1 with Zeise's Dimer in Ether (McQuillin's Experiment). A solution containing Zeise's dimer (0.038 g, 0.13 mmol) and **1** (0.049 g, 0.51 mmol) in ether was reacted at various temperatures (−10, 0, 23, and 34 °C). At −10 °C, the reaction took 3 days to complete while at 34 °C the reaction was complete in 1 h. An orange solid was obtained after the reaction period and rotoevaporation of the solvent at low temperature. After treatment with KCN (0.17 g, 0.052 mmol) in 2 mL of H_2O, the hydrocarbons were garnered from the mixture by extraction with chloroform. Analysis of these by ^1H NMR and MS showed the same results in each case as were obtained from a similar experiment with **2a** in ether (vida supra).

Reaction of 2a with KCN. To a solution containing KCN (0.021 g, 0.32 mmol) in 2 mL of H_2O was added 0.025 g of freshly prepared **2a** (0.07 mmol). After 1 h of stirring at 25 °C, all of **2a** had dissolved. The solutions was extracted with chloroform which, after drying, was analyzed by ^1H NMR revealing the virtually quantitative yield of **1**.

Reaction of 2b (L = Pyridine) with Triphenylphosphine. To a stirred solution of **2b** (0.05 g, 0.10 mmol) in pyridine was added triphenylphosphine (0.116 g, 0.46 mmol). After 2 h at room temperature a white precipitate had formed. The volatile components were then collected by rapid vacuum distillation revealing only hydrocarbon **1** in quantitative yield.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation and Johnson-Matthey for support of this research.

Registry No. **1c**, 1192-37-6; **1d**, 591-49-1; **1e**, 628-92-2; **1f**, 286-08-8; **2a**, 108296-73-7; **2b**, 108296-74-8; **2b** (L = 1/2 bpy), 113947-95-8; **6**, 591-48-0; **7**, 591-47-9; **9**, 1888-90-0; **10**, 1489-56-1; **11**, 1489-57-2; Zeise's dimer, 12073-36-8; triphenylphosphine, 603-35-0.

(10) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057.
(11) McQuillan, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.
(12) Christl, M. *Chem. Ber.* **1975**, *108*, 2781.
(13) Dias, J. R.; Djerassi, C. *Org. Mass Spectrom.* **1973**, *7*, 753.
(14) Wittig, G.; Schoellkopf, U. *Org. Synth.* **1960**, *40*, 66.
(15) Birch, A. J.; Subba Rao, G. S. R. *Aust. J. Chem.* **1970**, *23*, 1641.
(16) Babad, H.; Flemon, W.; Wood, J. B., III *J. Org. Chem.* **1967**, *32*, 2871.
(17) Gorfinkel, M. I.; Sosedkina, T. P.; Koptyug, V. A. *Zh. Obshch. Khim.* **1967**, *37*, 1448.
(18) Ruttiman, A.; Wick, A.; Eschenmoser, A. *Helv. Chim. Acta* **1975**, *58*, 1450.