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Metallacyclobutarenes from cyclopropa[*b*]naphthalene: reactions with rhodium(I), platinum(0) and palladium(0)

Peter J. Stang *, Linsheng Song,

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112 (U.S.A.)

and Brian Halton

Department of Chemistry, Victoria University of Wellington, P.O. Box 600, Wellington (New Zealand)

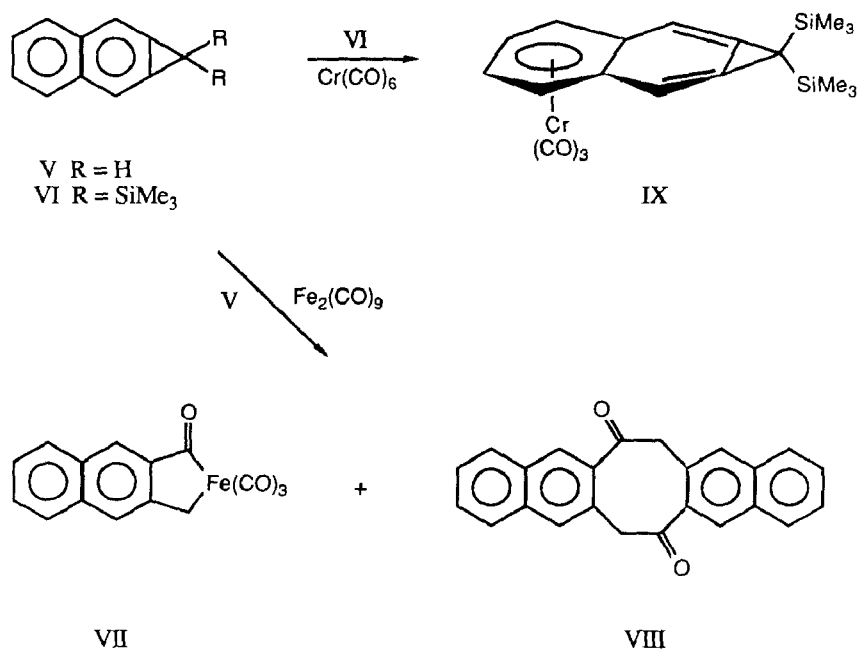
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Abstract

1*H*-Cyclopropa[*b*]naphthalene(V) reacts with chlorotris(triphenylphosphine)rhodium(I) and (ethene)bis(triphenylphosphine)platinum(0) with oxidative insertion of the metal into the three-membered ring σ -bond; rhodia- and platina-2*H*-cyclobuta[*b*]naphthalenes result. Tetrakis(triphenylphosphine)palladium(0) provides an unstable homologous product.

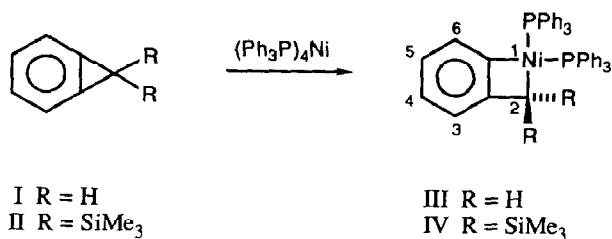
Introduction

While the chemistry of the cycloproparenes is now well established [1], the behavior of these highly strained aromatics with organometallic reagents has only recently attracted attention. Thus cyclopropabenzene(I) and its 1,1-bis(trimethylsilyl) derivative II react with, for example, tetrakis(triphenylphosphine)nickel(0) to give the ring expanded nickelacyclobutarenes III and IV, respectively [2,3]. The behavior of I, II and the *gem*-difluoro derivative towards organo-nickel and -palladium reagents is notably dependent upon the nature of the ligands present and a range of fascinating compounds has now been produced [2–7]. In contrast, little attention has been paid to the more stable and readily accessible [8] homologue cyclopropa[*b*]naphthalene (V). The compound reacts with diiron nonacarbonyl [9] with insertion of the metal and one ligand into the σ -bond to give VII (Scheme 1) which is accompanied by the demetallated cyclooctadienedione VIII. Like I [10], V fails [11] to form a sandwich compound with chromium carbonyl, but the disilyl VI reacts effectively [11] and IX-results (Scheme 1). The interaction of V with other



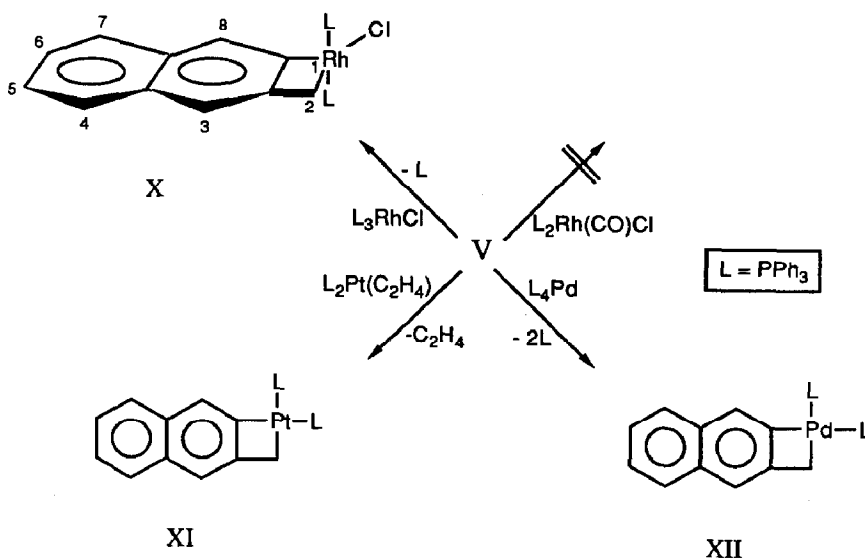
Scheme 1

organometallic reagents has not been described and we now provide the details of reactions with selected rhodium(I), platinum(0) and palladium(0) reagents.



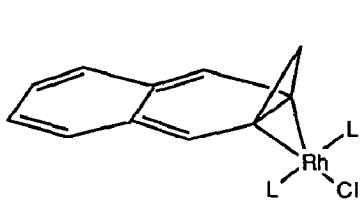
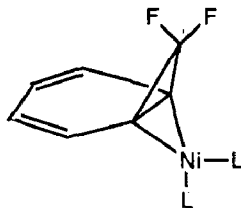
Results and discussion

The reaction of V with chlorotris(triphenylphosphine)rhodium [12] proceeds effectively to give an air-stable yellow powder in 74% yield. The compound corresponds to a 1/1 complex with the loss of one triphenylphosphine ligand and it is assigned as the rhodiacyclobutarene X (Scheme 2) primarily from its spectroscopic data. In particular, the ³¹P NMR spectrum displays only one doublet (¹J(Rh-P) 125.7 Hz) for the two phosphine ligands thereby establishing their magnetic equivalence. Not only is this fully consistent with X (in which the phosphines are located at the apical positions of the trigonal bipyramid about rhodium) but also it effectively eliminates propellane XIII, the product of oxidative addition of rhodium to the bridgehead HOMO of V. The appearance of XIII would be in strict analogy to the behavior of 1,1-difluorocyclopropabenzene with tetrakis(triphenylphosphine)nickel(0) which yields XIV [6]. In addition, the ¹H NMR spectrum shows the methylene group of X as a multiplet coupled to both rhodium



Scheme 2

and phosphorus (2.16 ppm, ${}^2J(\text{Rh}-\text{H}) \approx {}^3J(\text{P}-\text{H}) = 3.9$ Hz) and one aromatic proton is markedly shielded (H8 5.81 ppm). These data are incompatible with the bicyclobutane formulation XIII. In the ${}^{13}\text{C}$ NMR an aromatic methine resonance appears as a doublet (${}^2J(\text{Rh}-\text{C}2\text{a})$ 6.3 Hz) at 150 ppm. This is nicely consistent with the analogous signal for C2a of III and IV [2,3].

XIII L = PPh₃XIV L = PPh₃

The formation of X corresponds to oxidative insertion of the rhodium atom into the strained σ -bond of the cyclopropane and is directly analogous to the formation of the lower nickel homologues III and IV [2,3]. Addition to the strained bridge bond of V to give XIII requires loss of aromaticity in the remote ring and this is undoubtedly an unfavorable energetic process when compared with that for the formation of XIV. Because of the similarity in the behaviour of $\text{V} \rightarrow \text{X}$ to that of $\text{I} \rightarrow \text{III}$ [2] it was of interest to see if ring expansion with ligand insertion could also be induced, cf. $\text{V} \rightarrow \text{VII}$ [9]. Despite variations in the experimental conditions, the reaction between V and *trans*-carbonylbis(triphenylphosphine)rhodium(I) chloride, returned unchanged organometallic complex in high isolated (~84%) yield.

The behavior of V with (ethene)bis(triphenylphosphine)platinum(0) parallels that with Wilkinson's catalyst described above. The platinumacyclobutane XI is isolated as an air-stable, pale yellow powder in almost quantitative yield. The non-equivalence of the phosphorus ligands is shown by two distinct phosphorus doublets at 24.75 and 22.15 ppm (${}^1J(\text{Pt}-\text{P})$ 2067 and 1832 Hz, respectively) with ${}^{195}\text{Pt}$ satellites.

The CH₂ group (1.23 ppm) shows coupling to phosphorus (³J(P-H) 5 Hz) and to ¹⁹⁵Pt (²J(Pt-H) 79 Hz) and the pendant phenyl substituent(s) shield the proximal H8 proton (6.39 ppm) but not to the same extent as for H8 of X as is to be expected from the square planar geometry about platinum. H3 is also distinguished in this compound and resonates as a singlet at 6.79 ppm. These data are consistent only with the cyclobutarene formulation XI, the analogue of X, and not a platinapropellane equivalent to XIII. Reaction of V with tetrakis(triphenylphosphine)palladium(0) is readily effected (Experimental) but the product of reaction is very sensitive to both solvents (dichloromethane, chloroform) and air and has eluded formal characterization. However, the compound is tentatively assigned as XII on the basis of two distinct phosphorus resonances (27.7 and 22.8 ppm, ²J(P-P) 15 Hz) and the appearance of the methylene protons as a triplet at 1.60 ppm (³J(P-H) 6.6 Hz).

Concluding remarks

The behavior of cyclopropa[*b*]naphthalene with the platinum(0), palladium(0) and rhodium(I) complexes that have been examined is to yield the metallacyclobuta[*b*]naphthalenes X–XII. This is in direct analogy with the behavior of parent I with tetrakis(triphenylphosphine)nickel(0) and also the (cyclooctadiene)tris(tri-butyl-, -ethyl- and -phenyl-phosphine)nickel(0). On this basis the oxidative insertion of metals into the strained three-membered ring σ-bond of cycloproparenes is established as a general reaction for this class of highly strained aromatic hydrocarbons.

Experimental

General. All melting points are uncorrected and were recorded on a Mel-Temp capillary apparatus. Infrared spectra (cm⁻¹) were obtained for KBr pellets on a Matson Polaris FT-IR spectrometer. All NMR spectra were recorded on a Varian XL-300 spectrometer. ¹H chemical shifts were recorded at 299.69 MHz for chloroform-*d* solutions and are relative to internal tetramethylsilane (Me₄Si) (unless otherwise stated) while ¹³C spectra were measured at 75.43 MHz for dichloromethane-*d*₂ solutions and resonances are reported in ppm using the carbon resonance of the solvent (53.8 ppm) as standard. ³¹P data were obtained at 121.32 MHz for chloroform-*d* solutions with external 85% H₃PO₄ as standard at 0.0 ppm. Fast atom bombardment (FAB) mass spectra were measured with a VG Analytical 7050-E instrument employing chloroform/3-nitrobenzyl alcohol as the matrix.

Materials. Solvents were either reagent grade or were purified according to known procedures. Deuterated NMR solvents were purified by drying over calcium hydride and then vacuum transferred.

1*H*-Cyclopropa[*b*]naphthalene (V) was prepared according to the literature method [8]. Wilkinson's catalyst (tris(triphenylphosphine)rhodium(I) chloride) was prepared using the established procedure [12] as were *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) [13] and tetrakis(triphenylphosphine)palladium(0) [14]. (Ethene)bis(triphenylphosphine)platinum(0) [15] was prepared from platinum chloride as described below.

(Ethene)bis(triphenylphosphine)platinum(0) from PtCl_2

(a) Dichlorobis(triphenylphosphine)platinum(II). Platinum chloride (110 mg; 0.412 mmol) in degassed dimethyl sulfoxide (6 ml) was heated at 95°C under nitrogen and with stirring until a clear solution was obtained whereupon triphenylphosphine (325 mg; 1.24 mmol) was added in one portion and the heating continued for 4 min. The mixture was cooled to ambient temperature, ethanol (10 ml) added and the stirring continued for 10 min. The almost quantitative off-white precipitate of dichlorobis(triphenylphosphine)platinum(II) was filtered, washed with ethanol (4×4 ml) and ether (2×3 ml), dried and used without further purification.

(b) (Ethene)bis(triphenylphosphine)platinum(0). To a portion of the product from above (244 mg; 0.309 mmol) stirred in degassed ethanol (6 ml) and under nitrogen was bubbled ethene to effect saturation. Sodium borohydride (0.1 *M* in degassed ethanol, 9.3 ml) was slowly introduced from a syringe. The flow of ethene was continued throughout the addition and for a further 2 h. The off-white solid was filtered, washed with water (4×3 ml), ethanol (3×3 ml) and air dried to provide the desired complex (178 mg; 77%) identical to material prepared by the published procedure [15].

1-Chloro-1,1-bis(triphenylphosphine)-1-rhodia-2H-cyclobuta[b]naphthalene (X). To a solution of chlorotris(triphenylphosphine)rhodium(I) (149 mg; 0.161 mmol) in dichloromethane (3 ml, degassed) under nitrogen and at -23°C [$\text{CCl}_4/\text{CO}_2(\text{s})$] was added in one portion cyclopropa[b]naphthalene (V) (25 mg; 0.179 mmol). The mixture was stirred at -23°C for 5 min and then allowed to warm to ambient temperature over 40 min. Hexane (4 ml) was added and nitrogen was bubbled through the solution whereupon a yellow precipitate was slowly deposited. Additional hexane (~ 4 ml) was added, the precipitate filtered, and then washed with methanol (3×2 ml) and hexane (3×2 ml) to give X as a yellow powder (96 mg; 74%), m.p. $130\text{--}133^\circ\text{C}$ dec. (Found: C, 64.05; H, 4.47. $\text{C}_{47}\text{H}_{38}\text{P}_2\text{ClRh} \cdot 1.1 \text{CH}_2\text{Cl}_2$ calcd.: C, 64.44; H, 4.52.) IR 3052, 1481, 1435, 1265, 1187, 1096, 1028, 856, 742 and 693 cm^{-1} . ^1H NMR 7.42–7.34 (m; 12H), 7.31–7.22 (m; 10H), 7.20–7.05 (m; 13H), 5.81 (s; H8), 2.16 (dd; $^2J(\text{Rh-H}) \sim ^3J(\text{P-H}) = 3.9 \text{ Hz}$; CH_2). ^{13}C NMR: 150.0 (d; $^2J(\text{Rh-C2a})$ 6.3 Hz; C2a), 134.7 (12 CH), 130.1 (6 CH), 127.9(5) (12 CH), 133.0–127.2 (complex), 125.3, 124.3(5), 123.5, 122.6(5), 120.5, -2.9 (d; $^1J(\text{Rh-C2})$ 21 Hz; $^2J(\text{P-C2})$ not resolved; C2). ^{31}P NMR 32.9 (d; $^1J(\text{Rh-P})$ 125.7 Hz). *m/z* 802 (1; *M*), 767 (18; *M* – Cl), 627 (8; $\text{Rh}(\text{PPh}_3)_2$), 505 (28; $\text{C}_{11}\text{H}_8\text{RhPPh}_3$), 286 (100%; $\text{C}_{12}\text{H}_8\text{PRh}$).

1,1-Bis(triphenylphosphine)-1-platina-2H-cyclobuta[b]naphthalene (XI). To a mixture of cyclopropa[b]naphthalene (V) (74 mg; 0.529 mmol) and (ethene)bis(triphenylphosphine)platinum(0) (358 mg; 0.479 mmol) under nitrogen was added throughly degassed benzene (10 ml). The solution was heated to $50\text{--}55^\circ\text{C}$ with stirring and under nitrogen for 2 h. The pale yellow solution was filtered, the filtrate concentrated in vacuum and the residue crystallized from dichloromethane/hexane to afford XI as a pale yellow solid (377 mg; 92%), m.p. $171\text{--}173^\circ\text{C}$. (Found: C, 64.84; H, 4.46. $\text{C}_{47}\text{H}_{38}\text{P}_2\text{Pt} \cdot 0.11\text{CH}_2\text{Cl}_2$ calcd.: C, 65.10; H, 4.43%.) IR 3051, 1480, 1435, 1183, 1096, 742, 694 cm^{-1} . ^1H NMR 7.55–7.40 (m, 13H), 7.35–7.05 (m, 21H), 6.79 (s, H3), 6.39 (d (with ^{195}Pt satellites); $^4J(\text{P-H})$ 5 Hz; $^3J(\text{Pt-H})$ 73 Hz; H8), 1.23 (t (with ^{195}Pt satellites); $^3J(\text{P-H})$ 5 Hz; $^2J(\text{Pt-H})$ 79 Hz; CH_2). ^{13}C NMR 161.2 (t; $^3J(\text{P-C})$ 5.1 Hz; C2a), 134.7 (complex m; 12CH), 134–131 (complex), 129.9 (s, 6CH), 128.1–127.9 (12CH), 128.8–126.8 (complex m), 123.2, 122.9, 122.05 (dd;

$^2J(\text{P}-\text{C8a})$ 7.5 Hz; $^2J(\text{P}-\text{C8a})$ 3 Hz; C8a), -3.21 (dd; $^2J(\text{trans-P}-\text{C2})$ 82 Hz; $^2J(\text{cis-P}-\text{C2})$ 4 Hz; C2). ^{31}P NMR 24.75 (d (with ^{195}Pt satellites); $^1J(\text{Pt}-\text{P})$ 2067; $^2J(\text{P}-\text{P})$ 9 Hz), 22.15 (d (with ^{195}Pt satellites); $^1J(\text{Pt}-\text{P})$ 1832 Hz; $^2J(\text{P}-\text{P})$ 9 Hz). m/z 859 (24; M), 719 (26; $M - \text{C}_{11}\text{H}_8$), 597 (18; $M - \text{PPh}_3$), 457 (92; $\text{Pt}(\text{PPh}_3)$), 379(91), 302(36), 183(96%).

1,1-Bis(triphenylphosphine)-1-pallada-2H-cyclopropa[b]naphthalene (XII). To a mixture of cyclopropa[b]naphthalene (V) (20.4 mg; 0.146 mmol) and tetrakis(triphenylphosphine)palladium(0) (139 mg, 0.120 mmol) in a Schlenk flask (50 cm³) and under argon was added degassed toluene (5 ml). After stirring at room temperature for 2 h hexane (25 ml; dry and degassed) was added and the stirring continued for 1 h. The light yellow precipitate thus formed was filtered under nitrogen and dried in vacuum. The material, which darkens in air and decomposes almost instantly in chloroform and dichloromethane, is tentatively assigned as XII. ^1H NMR (C_6D_6) 7.70–7.58 (m; 4H), 7.56–7.35 (m; 8H), 7.24–7.13 (m; 2H), 7.06–6.76 (m, 22H), 1.60 (t; $^3J(\text{P}-\text{H})$ 6.6 Hz, CH_2). ^{31}P NMR (C_6D_6) 27.7 (d; $^2J(\text{P}-\text{P})$ 15 Hz), 22.8 (d; $^2J(\text{P}-\text{P}) = 15$ Hz).

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