

# Stepwise Transition Metal Promoted Ring Expansion Reactions of Vinylcyclopropanes to Give Cyclopentadienes and Cyclohexa-2,4-dienones. The First Example of a 1-Metallacyclohexa-2,4-diene Complex, $\{[\text{Pt}-\text{CH}_2-\text{CH}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{C}(\text{Ph})](\text{PPh}_3)_2\}$

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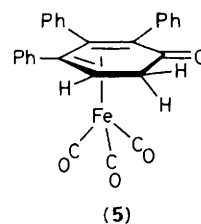
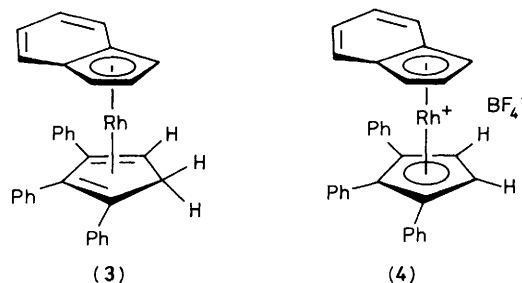
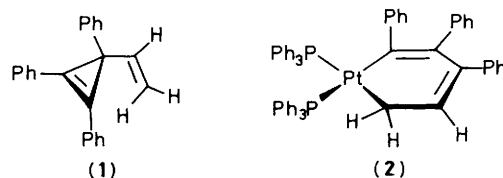
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1,2,3-Triphenyl-3-vinylcycloprop-1-ene (**1**) reacts with  $[\text{Pt}(\eta^2-\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  to give the first example of a 1-platinacyclohexa-2,4-diene complex (**2**) (the crystal structure of which has been determined), with  $[\text{Rh}(\eta^5-\text{C}_9\text{H}_7)(\eta-\text{C}_2\text{H}_4)_2]$  to give the  $\eta^4$ -cyclopentadiene compound (**3**), and with  $[\text{Fe}_2(\text{CO})_9]$  to give the  $\eta^4$ -cyclohexa-2,4-dienone complex (**5**); on heating, the metallacyclohexadiene (**2**) reductively eliminates 1,2,3-triphenylcyclopentadiene.

The transition metal chemistry of vinylcyclopropanes has been extensively studied and has provided considerable insight into the mechanisms of metal promoted carbon-carbon bond activation.<sup>1</sup> In contrast, the more highly unsaturated vinylcyclopropanes have received little attention, although reports of their photochemical<sup>2,3</sup> and thermal (180 °C)<sup>4</sup> ring expansion reactions to give substituted cyclopentadienes have appeared. Such reactions formally involve a thermally forbidden 1,3-sigmatropic shift of an  $\text{sp}^2$  carbon atom of the cyclopropene ring. We now report that these highly strained molecules undergo facile ring cleavage in the presence of transition metal complexes to form 1-metallacyclohexa-2,4-diene rings, and that such metallacycles appear to be intermediates *en route* to cyclopentadienes and cyclohexa-2,4-dienones.

1,2,3-Triphenyl-3-vinylcycloprop-1-ene (**1**)<sup>5,6</sup> reacts quantitatively with the 16-electron complex  $[\text{Pt}(\eta^2-\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  in  $\text{Et}_2\text{O}$  solution at room temperature to afford the bright yellow, air-stable  $\text{Pt}^{\text{II}}$  complex (**2**),<sup>†</sup> *via* a formal oxidative addition of the vinylcyclopropene to the  $\text{Pt}^0$  centre. This compound contains the first example of a 1-metallacyclohexa-2,4-diene ring, as shown by an X-ray diffraction study on a yellow single crystal grown from  $\text{Et}_2\text{O}$ . The

molecular structure of (**2**) is shown in Figure 1.‡ The metallacyclic ring is puckered, contains localised single and double bonds between carbon atoms, and shows no evidence of interaction of either olefinic bond with the co-ordinatively unsaturated metal centre. N.m.r. studies† demonstrate that



† Satisfactory microanalysis data ( $\text{C}, \text{H} \pm 0.3\%$  of calculated values) were obtained for (**2**)–(**5**).

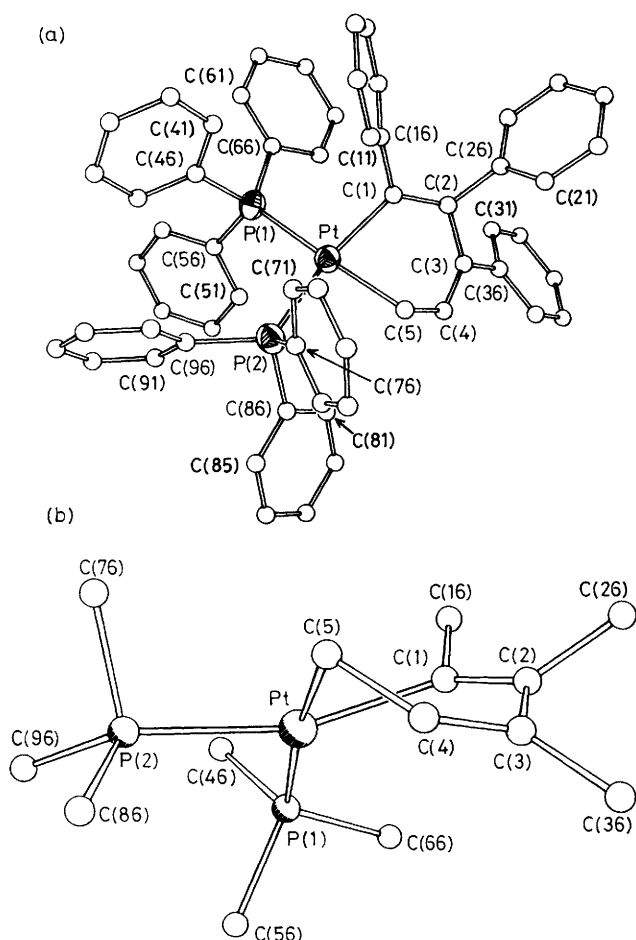
(**2**):  $^1\text{H}$  n.m.r. (300 MHz,  $\text{CDCl}_3$ ,  $J$  values in Hz):  $\delta$  1.87 [m ( $J_{\text{HH}} 2$ , 7;  $J_{\text{PH}} 60$ ;  $J_{\text{PH}} 18$ , 8), 1H,  $\text{CH}_2$ ], 4.00 [m ( $J_{\text{HH}} 6$ , 7;  $J_{\text{PH}} 132$ ;  $J_{\text{PH}} 13$ , 2), 1H,  $\text{CH}_2$ ], 6.40 [m ( $J_{\text{HH}} 6$ , 2;  $J_{\text{PH}} 6$ , 6), 1H, CH], 6.8–8.0 [m, 45H, Ph];  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.5 [dd,  $J_{\text{PC}} 80$ , 6,  $J_{\text{PtC}} 506$ ,  $\text{PtCH}_2$ ], 149.1 [d,  $J_{\text{PC}} 4$ ,  $J_{\text{PtC}} 127$ ,  $\text{PtCH}_2\text{CH}$ ], 162.5 [dd,  $J_{\text{PC}} 104$ , 10,  $J_{\text{PtC}} 1024$ ,  $\text{PtCPh}$ ], 123–143 [other resonances due to ring and Ph carbons could not be unambiguously assigned];  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. (121 MHz,  $\text{CDCl}_3$ , shifts relative to external  $\text{H}_3\text{PO}_4$ ):  $\delta$  23.7 [d ( $J_{\text{PP}} 5.4$ ,  $J_{\text{PtP}} 2129$ )], 21.3 [d ( $J_{\text{PP}} 5.4$ ,  $J_{\text{PtP}} 2119$ )] p.p.m.

(**3**):  $^1\text{H}$  n.m.r.:  $\delta$  3.08 [d,  $J$  13, 1H,  $\text{CH}_2$ ], 3.66 [d,  $J$  13, 1H,  $\text{CH}_2$ ], 4.02 [s, 1H, CH], 5.33 [s, 1H, indenyl CH], 5.81 [s, 1H, indenyl CH], 6.25 [s, 1H, indenyl CH], 6.5–7.3 [m, 19H, aromatic];  $^{13}\text{C}$  n.m.r.:  $\delta$  46.8 [t,  $J_{\text{CH}} 132$ ,  $\text{CH}_2$ ], 49.3 [d,  $J_{\text{CH}} 162$ , CH], 72.6 [d,  $J_{\text{CH}} 179$ , indenyl  $\text{CH}_{\text{terminal}}$ ], 82.5 [d,  $J_{\text{CH}} 171$ , indenyl  $\text{CH}_{\text{terminal}}$ ], 90.4 [d,  $J_{\text{CH}} 163$ , indenyl  $\text{CH}_{\text{internal}}$ ], 119.3 [d,  $J_{\text{CH}} 163$ , indenyl  $\text{CH}_{\text{aromatic}}$ ], 122.9 [d,  $J_{\text{CH}} 151$ , indenyl  $\text{CH}_{\text{aromatic}}$ ], 125–142.5 [aromatic].

(**4**):  $^1\text{H}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  5.31 [s, 1H, indenyl CH], 6.32 [s, 2H, indenyl CH], 6.40 [s, 2H, cyclopentadienyl CH], 6.8–7.5 [m, 19H, aromatic];  $^{13}\text{C}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  82.1 [d,  $J_{\text{CH}} 186$ , indenyl  $\text{CH}_{\text{terminal}}$ ], 85.0 [d,  $J_{\text{CH}} 203$ , cyclopentadienyl CH], 89.2 [d,  $J_{\text{CH}} 185$ , indenyl  $\text{C}-\text{H}_{\text{internal}}$ ], 105.0 [s, C-Ph], 108.3 [s, C-Ph], 123–132.7 [aromatics].

(**5**):  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  2.30 [dd,  $J$  19, 1.8, 1H,  $\text{CH}_2$ ], 2.70 [dd,  $J$  19, 4, 1H,  $\text{CH}_2$ ], 3.05 [dd,  $J$  4, 1.8, 1H, CH], 7–7.5 [m, 15H, Ph];  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  209.7 (Fe-CO), 194.9 (C=O), 137.2–126.0 (Ph), 111.2 (C-Ph), 104.5 (C-Ph), 84.2 (C-Ph), 51.4 (CH), 36.2 ( $\text{CH}_2$ ); i.r. (hexane)  $\nu_{\text{CO}}$  2060, 2005, 1993, 1690  $\text{cm}^{-1}$ .

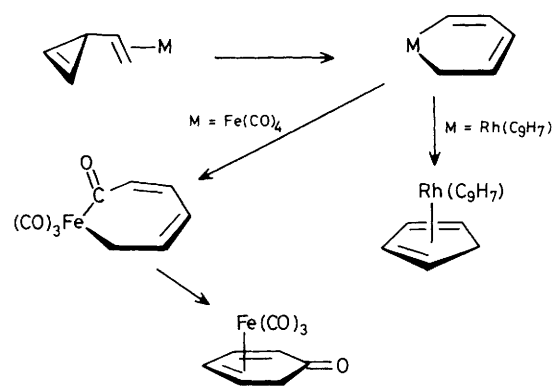
‡ Crystal Data: (23 °C) for (**2**), monoclinic, space group  $P2_1/n$ ,  $M = 1014.1$ ,  $a = 11.219(3)$ ,  $b = 17.989(5)$ ,  $c = 23.752(9)$  Å,  $\beta = 95.36(2)^\circ$ ,  $U = 4773(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.411$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo}-K\alpha) = 31.9$   $\text{cm}^{-1}$ . The Pt atom was located by heavy atom methods. A Nicolet R3m diffractometer was used to collect 6657 reflections ( $4^\circ \leq 2\theta \leq 45^\circ$ ) of which 6230 were unique and 4236 with  $F_o \geq 3\sigma(F_o)$  were considered observed. The intensity data were corrected for absorption ( $T_{\text{max}}/T_{\text{min}} = 1.13$ ). All non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms were treated as idealised isotropic contributions. The phenyl rings were constrained to rigid, planar, hexagonal groups, C–C = 1.395 Å. At convergence  $R(F) = 4.61\%$ ,  $R_w(F) = 5.21\%$ , G.O.F. = 1.008,  $\Delta/\sigma = 0.07$ ,  $\Delta(\rho) = 0.68$  e Å<sup>−3</sup>,  $N_o/N_v = 9.4$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.



**Figure 1.** (a) Molecular structure and labelling scheme for (2). (b) View of the metallacyclic ring with only the *ipso* carbon atoms of each phenyl ring shown for clarity. Pt–P(1), 2.306(3); Pt–P(2), 2.313(3); Pt–C(1), 2.088(9); Pt–C(5), 2.123(10); C(1)–C(2), 1.36(1); C(2)–C(3), 1.49(1); C(3)–C(4), 1.34(1); C(4)–C(5), 1.50(1) Å. P(1)–Pt–P(2), 99.3(1); P(1)–Pt–C(1), 96.2(3); P(1)–Pt–C(5), 173.2(3); P(2)–Pt–C(1), 160.8(3); P(2)–Pt–C(5), 85.1(3); C(1)–Pt–C(5), 80.6(4); Pt–C(1)–C(2), 124.6(7); C(1)–C(2)–C(3), 120.5(8); C(2)–C(3)–C(4), 117.9(9); C(3)–C(4)–C(5), 124.7(9); C(4)–C(5)–Pt, 106.1(6)°.

the metallacyclic structure is maintained in solution, and that the CH<sub>2</sub> protons are apparently inequivalent at room temperature, indicating the absence of rapid ring inversion. While (2) is thermally stable at room temperature, heating in C<sub>6</sub>D<sub>6</sub> solution causes slow reductive elimination of 1,2,3-triphenylcyclopentadiene,<sup>5,6</sup> with concomitant formation of the red cluster complex {[*o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PtPPh<sub>2</sub>]<sub>4</sub>}, a known degradation product of the [Pt(PPh<sub>3</sub>)<sub>2</sub>] fragment.<sup>7–9</sup>

No reaction between (1) and the 18-electron complex [Rh(η-C<sub>5</sub>Me<sub>5</sub>)(η-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] was observed in refluxing hexane, but the more labile η<sup>5</sup>-indenyl analogue [Rh(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)(η-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] reacts cleanly with (1) under these conditions to produce red crystals of the η<sup>4</sup>-cyclopentadiene complex (3).<sup>†</sup> As expected, subsequent reaction of (3) with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>–</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution results in hydride abstraction to give the cationic sandwich complex (4).<sup>†</sup> Contrasting behaviour is observed with the CO containing substrate [Fe<sub>2</sub>(CO)<sub>9</sub>], which reacts smoothly with (1) at room temperature in Et<sub>2</sub>O to afford the pale yellow crystalline η<sup>4</sup>-cyclohexa-2,4-dienone complex (5) in >90% yield.<sup>†</sup>



**Scheme 1**

These results demonstrate that initial, presumably olefinic, co-ordination of vinylcyclopropenes to low valent metal centres is followed rapidly by cleavage of a cyclopropene C–C bond to give metallacyclohexadiene compounds in a net oxidative addition reaction; subsequent reductive elimination affords the cyclopentadiene (Scheme 1). The overall reaction from the vinylcyclopropene constitutes a net 1,3-sigmatropic shift of a cyclopropene sp<sup>2</sup> carbon atom. A similar overall 1,3-shift of an sp<sup>2</sup> centre has been observed in the [Ni(CO)<sub>4</sub>] promoted ring expansion of a vinylcyclobutene to a cyclohexa-1,4-diene, but no metallacyclic intermediate was detected.<sup>10</sup> Our results imply that this reaction may also proceed in a stepwise fashion. In the Rh chemistry described above, we propose that initial ring opening to a metallacyclohexadiene occurs, but that subsequent thermal reductive elimination under the reaction conditions affords the co-ordinated cyclopentadiene ligand. The observed Fe chemistry suggests that in the presence of co-ordinated CO reductive elimination is preceded by CO insertion (Scheme 1). Such oxidative addition of vinyl cyclopropenes to low valent metal centres should provide a general route to these novel metallacyclohexadiene compounds.

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