

Cleavage of Carbon-Carbon Bonds in a Cyclopropene Derivative by Platinum Complexes

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O composto 1,2-difenil-3-(dicianometileno)ciclopropeno (TRYA) sofre a quebra da ligação dupla carbono-carbono em reações com $[\text{Pt}_3(\text{CNBu}^t)_6]$ (nas razões molares de 2:1 e 1:1) e $[\text{Pt}(\text{COD})_2]$ (na razão molar de 2:1), originando-se complexos propanodilidenodiplatina $[\text{Pt}_2\{\mu\text{-}(\text{PhC})_2\text{C}=\text{C}(\text{CN})_2\}(\text{CNBu}^t)_4]$ (**1a**) e $[\text{Pt}_2\{\mu\text{-}(\text{PhC})_2\text{C}=\text{C}(\text{CN})_2\}(\text{COD})_2]$ (**1b**) (COD = 1,5-ciclooctadieno). No entanto, as reações de abertura anelar do TRYA com quantidades equimolares de $[\text{Pt}(\text{PR}_3)(\text{C}_2\text{H}_4)_2]$ (R = Ph, e Cy) conduzem à inserção da platina na ligação simples carbono-carbono, formando-se platinaciclobutenos dinucleares $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PR}_3)]_2$ (**2a**, R = Ph e **2b**, R = Cy). Os complexos **2a** e **2b** tratados com 2 e 4 equivalentes de CNBu^t dão os correspondentes complexos mononucleares $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PR}_3)(\text{CNBu}^t)]$ (**3a**, R = Ph e **3b**, R = Cy) e $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{CNBu}^t)_2]$ (**3c**). A reação do $[\text{Pt}(\text{COD})_2]$ com 1 equivalente do TRYA produz o platinaciclobuteno $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{COD})]$ (**3d**). Além disso, os ligantes COD deslocam-se prontamente de **1b** e **3d** pela adição de um excesso de CNBu^t , fornecendo **1a** e **3c**.

The compound 1,2-diphenyl-3-(dicyanomethylene)cyclopropene (TRYA) undergoes carbon-carbon double bond cleavage in reactions with $[\text{Pt}_3(\text{CNBu}^t)_6]$ (in 2:1 and 1:1 mol ratios) and $[\text{Pt}(\text{COD})_2]$ (in 2:1 mol ratio), to give the propanediylidenediplatinum complexes $[\text{Pt}_2\{\mu\text{-}(\text{PhC})_2\text{C}=\text{C}(\text{CN})_2\}(\text{CNBu}^t)_4]$ (**1a**) and $[\text{Pt}_2\{\mu\text{-}(\text{PhC})_2\text{C}=\text{C}(\text{CN})_2\}(\text{COD})_2]$ (**1b**) (COD = 1,5-cyclooctadiene). However, ring-opening reactions of TRYA with equimolar amounts of $[\text{Pt}(\text{PR}_3)(\text{C}_2\text{H}_4)_2]$ (R = Ph, and Cy) lead to the insertion of the platinum into the single carbon-carbon bond, forming dinuclear platinacyclobutenes $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PR}_3)]_2$ (**2a**, R = Ph and **2b**, R = Cy). Complexes **2a** and **2b**, treated with 2 and 4 equivalents of CNBu^t , give the related mononuclear platinacyclobutenes $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PR}_3)(\text{CNBu}^t)]$ (**3a**, R = Ph and **3b**, R = Cy) and $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{CNBu}^t)_2]$ (**3c**). The reaction of $[\text{Pt}(\text{COD})_2]$ with 1 equivalent of TRYA produces the platinacyclobutene $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{COD})]$ (**3d**). Furthermore, the COD ligands are readily displaced from **1b** and **3d** by the addition of an excess of CNBu^t , to afford **1a** and **3c**.

Keywords: cyclopropene, platinum complexes, ring-opening, platinacyclobutene

Introduction

There are extensive examples of catalytic reactions involving the metal-promoted activation of carbon-carbon bonds of cyclopropenes in the literature¹. Metallacyclobutenes² and bridged carbene complexes³ have been isolated either from ring-opening reactions of cyclopropenes, or indirectly from alkyne-carbene complexes coupling at the metal⁴. The thermal stability of unsaturated three-membered carbocycles is markedly enhanced by electron-withdrawing groups such as oxygen and dicyanomethylene at C-3, which stabilize a dipolar form with a relatively large positive charge on the C₃ atoms⁵. Stoichiometric reactions of such methylenecyclopropenes with platinum complexes often result in the insertion of the metal into the carbon-carbon single bond of the three membered-ring with the formation of platinacyclobutene rings^{6,7,8,9}. Cleavage reactions of the C=C link have only been observed in diphenylcyclopropenone, accomplished by [Pt₃(CNBu^t)₆] and [Pt(COD)(mvk)] (mvk = methyl vinyl ketone), to give μ -2-oxo-1,3-diphenylpropanediylidene complexes [Pt₂{ μ ₂(PhC)₂CO}L₄] (L = CNBu^t and L₂ = COD), where the two PtL₂ groups are bridged transversely by a perpendicular PhCC(O)CPh fragment¹⁰. An interpretation of the emerging results was also the subject of a theoretical study¹¹.

Herein we report a systematic study focusing on the reactions between TRYA and platinum complexes, in which the TRYA undergoes both carbon-carbon single and double bond cleavages to give platinacyclobutenes and propanediylidenediplatinum complexes.

Experimental Details

General Considerations

C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Melting points were measured in air on a Mettler EP52 apparatus and are uncorrected. Molecular weight determinations in solution at three or more different concentrations were obtained on a Knauer Vapor-Pressure Osmometer. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 337 spectrophotometer, and proton NMR spectra on a Varian XL100 spectrometer at 100.1 MHz, on a Bruker AW80 spectrometer at 80 MHz, or on a Bruker AC300 spectrometer at 300.13 MHz. ¹³C-{¹H} NMR spectra were recorded on a Varian XL100 at 25.2 MHz or on a Bruker AC300 spectrometer at 75.47 MHz, and ³¹P-{¹H} NMR spectra on a Bruker AC300 spectrometer at 121.5 MHz. NMR spectra were recorded in CDCl₃ and chemical shifts are quoted with respect to tetramethylsilane (¹H and C¹³) and 85% phosphoric acid (³¹P) as an external reference without corrections for diamagnetic susceptibilities.

Experiments were carried out under a dry, oxygen-free, argon atmosphere using solvents which were dried and distilled under argon before use. Light petroleum refers to the fraction of b.p. 40–60 °C. Chromatographies were performed over Merck GF₂₅₄ silica gel. The reagents CNBu^t¹² and TRYA¹³, and the complexes [Pt(COD)₂], [Pt₃(CNBu^t)₆], and [Pt(PR₃)(C₂H₄)₂] (R = Ph and Cy)¹⁴ were prepared as described in the literature. Other reagents were used as obtained from commercial sources.

The preparation of propanediylidenediplatinum complexes

(a) [Pt₂{ μ ₂(PhC)₂C=C(CN)₂}(CNBu^t)₄] (**1a**)

(i) TRYA (0.080 g, 0.315 mmol) was added to a stirred solution of [Pt₃(CNBu^t)₆] (0.228 g, 0.210 mmol) in THF (15 mL), and the mixture was stirred for 3 h. Filtration of the solution on a short alumina column and evaporation to 3 mL followed by the addition of ethyl ether afforded yellow microcrystals of **1a** (0.111 g, 36%). Anal. Calcd. for C₃₈H₄₆N₆Pt₂: C, 46.7; H, 4.7; N, 8.6. Found: C, 46.5; H, 4.8; N, 8.3%. Mp 270 °C dec; mol wt. (CHCl₃), found: 988, calcd. 977. IR; ν (CN) at 2195 w, 2185 s and 2155 s cm⁻¹. NMR: ¹H (100.1 MHz), δ 7.62–7.23 (m, 10 H, Ph) and 1.40 (s, 36 H, ^tBu); ¹³C-{¹H} (25.2 MHz), δ 160.2 [s, C=C(CN)₂], 44.0 (s, Ph, C_{ipso}), 129.9 (s, Ph, C_o), 126.9 (s, CNBu^t), 125.5 (s, Ph, C_m), 124.4 (s, Ph, C_p), 120.1 [s, C=C(CN)₂, J(PtC) 16 Hz], 86.8 [C=C(CN)₂], 80.4 [s, C₂C=C(CN)₂, ¹J(PtC) 558 Hz], 56.6 (s, C, Bu^t), 29.2 (s, Bu^t).

(ii) The reaction between TRYA (0.076 g, 0.30 mmol) and [Pt₃(CNBu^t)₆] (0.108 g, 0.10 mmol) was performed as described above to yield **1a** (0.056 g 38%). Anal. Calcd. for C₃₈H₄₆N₆Pt₂: C, 46.7; H, 4.7; N, 8.6. Found: C, 46.3; H, 4.6; N, 8.4. %. The IR and ¹H-NMR data were identical to (i).

(iii) A solution of CNBu^t (0.02 cm³, 0.18 mmol) in THF (2 mL) was added dropwise to a solution of **1b** (0.05 g, 0.058 mmol) in THF (10 mL) at 0 °C. The solution was stirred for 3 h at room temperature and reduced to 2 cm³ under vacuum. Ethyl ether was added to give a residue, which was washed with the same solvent and dried to give yellow microcrystals of the complex **1a** (0.034 g, 61%). The IR and NMR data were identical to (I).

(b) [Pt₂{ μ ₂-(PhC)₂C=C(CN)₂}(COD)₂] (**1b**)

TRYA (0.063 g, 0.25 mmol) was added to a stirred solution of [Pt(COD)₂] (0.205 g, 0.50 mmol) in THF (15 mL) at 0 °C. After 10 min, the mixture was allowed to warm to room temperature and then stirred for 4 h. The volume was reduced to 3 mL. Ethyl ether was added to give an orange residue, which was then washed with the same solvent and dried. Chromatography of this residue on silica gel with hexane/ethyl acetate (30/70) and evaporation of the solvents afforded orange microcrystals of **1b** (0.074 g, 35%). Anal. Calcd. for C₃₄H₃₄N₂Pt₂: C, 47.4; H, 4.0; N, 3.2.

Found: C, 46.7; H, 4.2; N, 2.8%. Mp 200 °C dec. IR: $\nu(\text{CN})$ at 2170 m and 2130 m cm^{-1} . NMR: ^1H (80 MHz), δ 7.60–6.68 (m, 10 H, Ph), 6.60–4.30 [m, 8 H, CH, COD, $J(\text{PtH})$ not discernible], and 2.90–2.00 (m, 16 H, CH_2 , COD); ^{13}C - $\{^1\text{H}\}$ (25.2 MHz), δ 165.4 [s, $\text{C}=\text{C}(\text{CN})_2$], 139.6 (s, Ph, C_{ipso}), 128.5 (s, Ph, C_o), 128.4 (s, Ph, C_m), 127.9 (s, Ph, C_p), 117.6 [s, $\text{C}=\text{C}(\text{CN})_2$], 99.3 [$\text{C}=\text{C}(\text{CN})_2$], 97.2 [s, $\text{C}_2\text{C}=\text{C}(\text{CN})_2$, $^1J(\text{PtC})$ not discernible], 95.5 [s, $\text{C}=\text{C}$, COD, $J(\text{PtC})$ 95 Hz], 93.6 [s, $\text{C}=\text{C}$, COD, $J(\text{PtC})$ 119 Hz], 31.0 (s, CH_2 , COD), and 28.0 (s, CH_2 , COD).

The preparation of dinuclear platinacyclobutene complexes

(a) $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PPh}_3)]_2$ (**2a**)

$[\text{Pt}(\text{PPh}_3)(\text{C}_2\text{H}_4)_2]$ (0.110 g, 0.216 mmol) was added portionwise to a stirred suspension of TRYA (0.054 g, 0.216 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred for 3 days at room temperature. The mixture was filtered through a short alumina column and the volume was reduced to 3 mL. Ethyl ether was added to give a yellow residue, which was then washed with the same solvent and dried. The solid was recrystallized from benzene-methanol to yield yellow microcrystals of **2a** (0.148 g, 96%). (Found: C, 60.71; H, 3.70; N, 3.33. $\text{C}_{72}\text{H}_{50}\text{N}_4\text{P}_2\text{Pt}_2$ requires C, 60.76; H, 3.54; N, 3.94%), m.p. 287–290 °C dec. Mol wt. (THF), found: 379, calcd. $1423/4 = 356$. IR $\nu(\text{CN})$ at 2210 s and 2190 m cm^{-1} . NMR: ^1H (100.1 MHz), δ 8.10–6.85 (m, 20 H, Ph), and 6.80–6.15 (m, 5 H, Ph).

(b) $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PCy}_3)]_2$ (**2b**)

$[\text{Pt}(\text{PCy}_3)(\text{C}_2\text{H}_4)_2]$ (0.246 g, 0.464 mmol) was added portionwise to a stirred suspension of TRYA (0.118 g, 0.464 mmol) in THF (15 mL), and the mixture was stirred for 3 days. The volume was reduced to 3 mL and ethyl ether was added to give a yellow precipitate. The residue was separated by thin-layer chromatography on silica gel with hexane-ethyl acetate (30:70), and then with hexane-ethyl acetate-methanol (50:25:25), and after recrystallization from dichloromethane-hexane afforded yellow microcrystals of **2b** (0.192 g, 28%). (Found: C, 57.46; H, 5.86; N, 3.57. $\text{C}_{72}\text{H}_{86}\text{N}_4\text{P}_2\text{Pt}_2$ requires C, 59.25; H, 5.94; N, 3.84%), mp 267–275 °C dec. Mol. wt. (trichloroethylene), found: 650, calcd. $1460/2 = 730$. IR $\nu(\text{CN})$ at 2227 m and 2200 m cm^{-1} . NMR: ^1H (100.1 MHz, CD_2Cl_2), δ 7.40–6.75 (m, 10 H, Ph), and 2.13–0.68 (m, 33 H, CH_2 , Cy).

The preparation of mononuclear platinacyclobutene complexes

(a) $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PPh}_3)(\text{CNBu}^t)]$ (**3a**)

CNBu^t (0.023 g, 0.281 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of **2a** (0.20 g, 0.140 mmol) in the same solvent (15 mL) at 0 °C. After 35 min, the mixture was allowed to warm to room temperature, stirred for 1.5 h, and filtered through a short alumina column. The volume was reduced to 3 mL and light petro-

leum was added to give a precipitate, which was then chromatographed over silica gel with hexane-ethyl acetate (40:30). Recrystallization from dichloromethane-methanol gave a pale yellow microcrystalline solid of **3a** (0.155 g, 69%). (Found: C, 62.31; H, 4.24; N, 4.93. $\text{C}_{41}\text{H}_{34}\text{N}_3\text{PPt}$ requires C, 61.95; H, 4.31; N, 5.29%), mp 176 °C. Mol wt. (CHCl_3), found: 824, calcd. 794. IR $\nu(\text{CN})$ at 2210 m and 2185 s cm^{-1} . NMR: ^1H (80 MHz), δ 7.90–6.90 (m, 20 H, Ph), 6.73–6.15 (m, 5 H, Ph), and 1.10 (s, 9 H, Bu^t); ^{13}C - $\{^1\text{H}\}$ (75.7 MHz), δ 168.5 [d, $\text{C}(\text{Ph})$, $^2J(\text{PtC}) = 89$ Hz], 163.5 [d, $\text{PtCC}(\text{CN})_2$, $^1J(\text{PtC}) = 638$ Hz, $^2J(\text{PC}) = 109$ Hz], 158.7 [s, $\text{PtC}(\text{Ph})$, $^1J(\text{PtC}) = 647$ Hz], 141.0 [d, Ph, TRYA, C_{ipso} , $^3J(\text{PtC}) = 37$ Hz, $^4J(\text{PC}) = 3$ Hz], 136.4 [d, Ph, TRYA, $^2J(\text{PtC}) = 97$ Hz, $^3J(\text{PC}) = 3$ Hz], 134.2–27.0 (Ph, PPh_3 and TRYA), 126.5 [s, CNBu^t , $^1J(\text{PtC}) = 1090$ Hz], 120.7 [d, $\text{C}:\text{C}(\text{CN})_2$, $^3J(\text{PtC}) = 75$ Hz, $^4J(\text{PC}) = 6$ Hz], 116.0 [d, $\text{C}:\text{C}(\text{CN})_2$, $^3J(\text{PtC}) = 114$ Hz, $^4J(\text{PC}) = 13$ Hz], 70.6 [d, $\text{C}(\text{CN})_2$, $^2J(\text{PtC}) = 40$ Hz, $^3J(\text{PC}) = 10$ Hz], 58.1 (s, C, Bu^t), 29.1 (s, CH_3 , Bu^t); ^{31}P - $\{^1\text{H}\}$ (121.5 MHz), δ 16.31 [s, $^1J(\text{PtP}) = 2181$ Hz].

(b) $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{PCy}_3)(\text{CNBu}^t)]$ (**3b**)

CNBu^t (0.018 g, 0.213 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of **2b** (0.155 g, 0.106 mmol) in the same solvent (15 mL) at 0 °C. After 30 min, the mixture was allowed to warm to room temperature and stirred for 1 h. The volume was reduced to 3 mL and light petroleum was added to give a precipitate, which was recrystallized from dichloromethane-light petroleum to give a pale yellow microcrystalline solid of **3b** (0.109 g, 63%). (Found: C, 61.50; H, 6.45; N, 5.24. $\text{C}_{41}\text{H}_{52}\text{N}_3\text{PPt}$ requires C, 60.56; H, 6.45; N, 5.17%). Mp 274 °C dec. Mol wt. (CHCl_3), found: 837, calcd. 812. IR $\nu(\text{CN})$ at 2205s, 2200 w, and 2180 s cm^{-1} . NMR: ^1H (100 MHz), δ 7.27–6.80 (m, 10 H, Ph), 1.61 (s, 9 H, Bu^t) and 2.13–0.68 (m, 33 H, CH_2 , Cy); ^{13}C - $\{^1\text{H}\}$ (25.2 MHz), δ 170.3 [s, $\text{C}(\text{Ph})$], 167.7 [d, $\text{PtCC}(\text{CN})_2$, $^1J(\text{PC}) = 100$ Hz], 160.5 [s, $\text{PtC}(\text{Ph})$], 143.2 [s, Ph, C_{ipso} , $^3J(\text{PtC}) = 42$ Hz], 136.5 [s, Ph, C_{ipso} , $^2J(\text{PtC}) = 84$ Hz], 128.9–25.6 (Ph, TRYA), 120.6 and 116.3 [s, $\text{C}(\text{CN})_2$], 58.5 [s, C, Bu^t], 48.6 [s, $\text{C}(\text{CN})_2$], 33.7 [d, CH, Cy, $^2J(\text{PtC}) = 18$ Hz, $^1J(\text{PC})$ 24 Hz], 29.8 [d, CHCH_2 , Cy, $^2J(\text{PC}) = 12$ Hz], 29.7 (s, Bu^t), 27.2 [d, CHCH_2CH_2 , Cy, $^3J(\text{PC}) = 11$ Hz], and 26.1 (s, CH_2 , Cy).

(c) $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}=\text{C}(\text{CN})_2(\text{CNBu}^t)_2]$ (**3c**).

(i) The reaction of **3d** with an excess of tert-butyl isocyanide

CNBu^t (0.17 g, 2 mmol) was added dropwise to a stirred solution of **3d** (0.352 g, 0.63 mmol) in THF (15 mL) at 0 °C. After 10 min, the mixture was allowed to warm to room temperature and then stirred for 30 min. The volume was reduced to 3 mL and ethyl ether was added to give a precipitate, which was washed with the same solvent and dried, giving a yellow microcrystalline solid of **3c** (0.302 g, 78%). (Found: C, 53.94; H, 4.80; N, 9.38. $\text{C}_{28}\text{H}_{28}\text{N}_4\text{Pt}$

requires C, 54.62; H, 4.59; N, 9.10%), mp 185 °C dec. Mol. wt. (CHCl₃), found: 689, calcd. 615. IR ν (CN) at 2220 s, 2210 w, 2190 s and 2160 w cm⁻¹. NMR: ¹H (300.13 MHz), δ 7.35–7.10 (m, 10 H, Ph), 1.59 (s, 9 H, Bu^t) and 1.45 (s, 9 H, Bu^t); ¹³C-¹H (75.47 MHz), δ 167.3 [s, C(Ph), ²J(PtC) = 84 Hz], 157.7 [s, PtCC(CN)₂, ¹J(PtC) = 677 Hz], 154.9 [s, PtC(Ph), ¹J(PtC) = 630 Hz], 140.7 [s, Ph, C_{ipso}, ³J(PtC) = 29], 136.9 [s, Ph, C_{ipso}, ¹J(PtC) = 99 Hz], 129.0–127.0 (Ph, TRYA), 128.4 [s, CNBu^t, ¹J(PtC) = 983 Hz], 120.5 [s, C(CN)₂, ³J(PtC) = 81 Hz], 115.8 [s, C(CN)₂, ³J(PtC) = 117 Hz], 71.3 [s, C(CN)₂, ²J(PtC) = 38 Hz], 58.1 [s, C, Bu^t], 30.0 and 29.7 (s, CH₃, Bu^t).

(ii) The reaction of **2a** with an excess of tert-butyl isocyanide

Complex **2a** (0.200 g, 0.141 mmol) was added portionwise to a stirred solution of CNBu^t (0.03 g, 0.363 mmol) in light petroleum (15 mL). The mixture was stirred for 3 h at room temperature and the supernatant liquid removed. The precipitate was washed with light petroleum and dried. Recrystallization from dichloromethane-light petroleum gave a yellow microcrystalline solid of complex **3c** (0.138 g, 80%). The IR and NMR data were identical to (i).

(iii) The reaction of **2b** with an excess of tert-butyl isocyanide

Complex **2b** (0.207 g, 0.142 mmol) was added portionwise to a stirred solution of CNBu^t (0.03 g, 0.363 mmol) in THF (15 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C and filtered through a short alumina column. The volume was reduced to 3 mL and light petroleum was added to give a yellow solid, which was washed with ethyl ether and light petroleum. Recrystallization from THF/light petroleum gave a yellow microcrystalline solid of **3c** (0.165 g, 95%). The IR and NMR data were identical to (i).

(d) [PtC(Ph)=C(Ph)C=C(CN)₂(CDO)] (**3d**)

TRYA (0.191 g, 0.75 mmol) was added to a stirred solution of [Pt(COD)₂] (0.308 g, 0.75 mmol) in THF (15 mL) at 0 °C. After 40 min, the mixture was allowed to warm to room temperature and stirred for 3 h to give a red solution. The volume was reduced to 3 mL and ethyl ether was added to give an orange precipitate which was washed with the same solvent and then dried. The product was chromatographed over silica gel with hexane-dichloromethane (50:50) to afford a pure sample of **3d** (0.375 g, 90%). (Found: C, 55.38; H, 4.10; N, 5.06. C₂₆H₂₂N₂Pt requires C, 56.00; H, 3.98; N, 5.03%), mp 230 °C dec. IR ν (CN) at 2210m and 2200 w cm⁻¹. NMR: ¹H (80 MHz), δ 7.90–6.90 (m, 10 H, Ph), 6.36 [s, 2 H, CH, COD, *J*(PtH) = 44 Hz], 5.30 [s, 2 H, CH, COD, *J*(PtH) = 48 Hz], and 2.90–2.00 (m, 8 H, CH₂, COD); ¹³C-¹H (75.7 MHz), δ 167.2 [s, C(Ph)], 156.7 [s, PtCC(CN)₂], 155.0 [s, PtC(Ph)], 139.4 [s, Ph, C_{ipso}, ³J(PtC) = 24 Hz], 134.3 [s, Ph, C_{ipso}, ²J(PtC) = 113 Hz], 130–126 (Ph, TRYA), 119.3 and 116.7 [s, C(CN)₂], 103.9 [s, CH, COD, ¹J(PtC) = 64 Hz], 103.8

[s, CH, COD, ¹J(PtC) = 46 Hz], 71.4 [s, C(CN)₂], 30.2 (s, CH₂, COD). 29.3 (s, CH₂, COD).

Results and Discussion

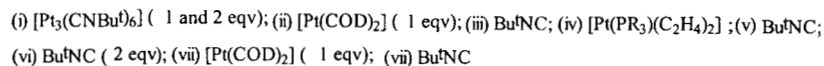
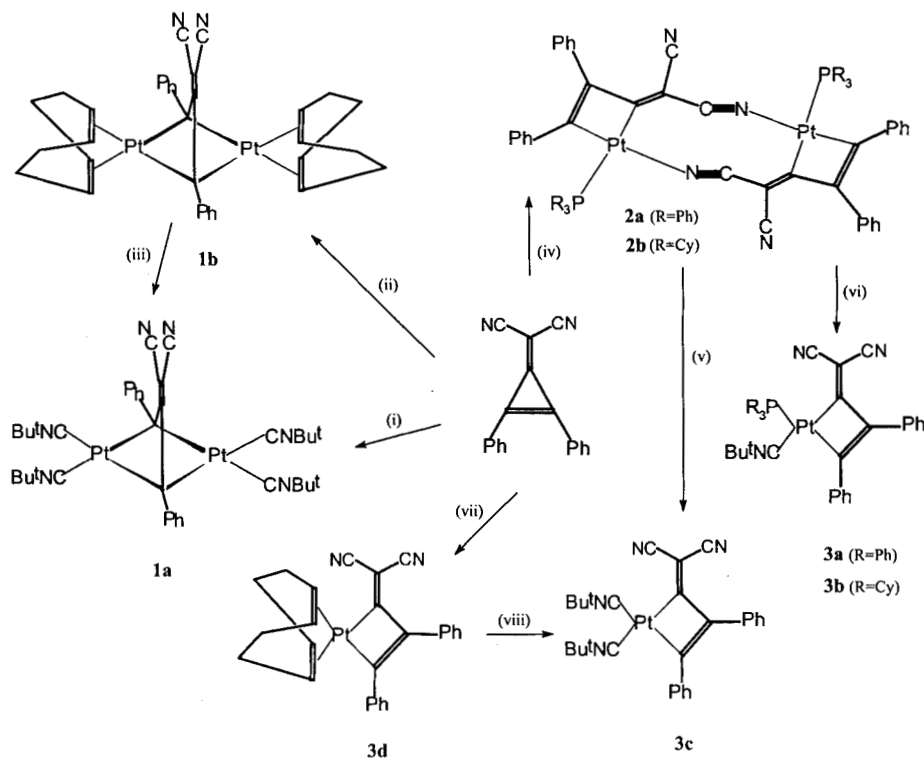
The synthesis and properties of the complexes

The propanediylidene [Pt₂{ μ_2 - (PhC)₂C=C(CN)₂} (CNBu^t)₄] (**1a**) was selectively prepared by reacting a THF solution of the cluster [Pt₃(CNBu^t)₆] with TRYA in 1:2 and 1:1 molar ratios, or by reaction of [Pt₂{ μ_2 - (PhC)₂C=C(CN)₂} (COD)₂] (**1b**) with an excess of CNBu^t. The formation of complex **1b** depends on the reactant ratios, requiring 2 equivalents of [Pt(COD)₂]. Otherwise, the product will be the platinacyclobutene **3d**. The dinuclears [PtC(Ph)=C(Ph)C=C(CN)₂(PR₃)₂] (**2a**, R = Ph and **2b**, R = Cy) are formed in good yield by the reactions of [Pt(PR₃)(C₂H₄)₂] (R = Cy and Ph) with TRYA in THF solutions. They are good starting materials for the preparation of mononuclear platinacyclobutenes because of the weak connection between the cyano group of TRYA and the fourth coordination site of the platinum atom. When **2a** and **2b** were treated with 1 equivalent of CNBu^t in THF they gave [PtC(Ph)=C(Ph)C=C(CN)₂(PPh₃)(CNBu^t)] (**3a**) and [PtC(Ph)=C(Ph)C=C(CN)₂(PCy₃)(CNBu^t)] (**3b**), respectively. The displacement of phosphine ligands from **2a** and **2b** with an excess of isocyanide also occurs, affording [PtC(Ph)=C(Ph)C=C(CN)₂(CNBu^t)₂] (**3c**). The related complex [PtC(Ph)=C(Ph)C=C(CN)₂(COD)] (**3d**) is straightforwardly prepared by reacting [Pt(COD)₂] with 1 equivalent of TRYA. Additional evidence for the formulation of **3d** is the formation of **3c** through the ready replacement of the COD ligand by two CNBu^t. The chemistry is summarized in the Scheme 1.

All complexes are stable in air in the solid state. Molecular weight measurements of dinuclear complexes show the dissociation of **2b** into two fragments in trichloroethylene, and the dissociation of **2a** into four species in THF. However, mononuclear complexes **3a**, **3b**, and **3c** retain their identity in chloroform. These results show that the tendency towards the rupture of the weak Pt—NC bond is greater than the dissociation of the phosphine ligand. In previous reactions of [Pt(PPh₃)₂(C₂H₄)] with TRYA carried out in THF only, the dinuclear complex was obtained^{8,9}. It seems that steric hindrance exerted by the phosphine ligand and coordinating solvent on the C(CN)₂ group favor the formation of the less strained dinuclear complex.

NMR spectroscopic characterizations

Complexes **1a** and **1b** exhibit the expected NMR (¹H, and ¹³C-¹H) spectroscopic features like those of μ_2 -oxo-1,3-diphenylpropanediylidene [Pt₂{ μ_2 -(PhC)₂CO}L₄]₁₀. The ¹H-NMR spectrum of **1a** displays characteristic signals of the phenyl protons in the range of 7.63–7.23 ppm, and a



Scheme 1.

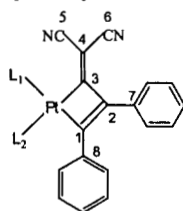
single sharp resonance of the But groups at 1.40 ppm. The phenyl signals of **1b** are observed in the range of 7.60–6.68 ppm, and two sets of COD resonances appear at 6.60–4.30 (CH) and 2.90–2.00 ppm (CH₂). Chemical shifts of **1a** at 160.2 and 80.4 ppm and **1b** at 165.4 and 97.2 ppm in the ¹³C-NMR spectra are assigned to the carbons of the C₃ ring. Satellites due to couplings to platinum-195 centered at 80.4 ppm for **1a**, with large ¹J(PtC) = 558 Hz, reflect the strength of the Pt–C(1)C(3) bonds.

The ¹H-NMR spectra of **3c** and **3d** show the presence of two non-equivalent isocyanide and COD ligands. Quaternary carbons CN of the isocyanide ligands of **3a** and **3c** appear in the ¹³C-NMR spectra at 126.4 and 128.5 ppm in the aromatic region with ¹J(PtC) 983 and 1090 Hz, respectively.

Table 1 summarizes the relevant ¹³C-¹H NMR data for the platinumacyclobutenes. The assignment of the quaternary carbons of the PtTRYA unit was mainly based on the ¹⁹⁵Pt-¹³C and ³¹P-¹³C spin coupling patterns of the more soluble **2a** and **3c**.

All the platinumacyclobutene monomers show two sets of chemical shifts for C-6 and C-5 around 116 [³J(PtC) = 114–117 Hz and ⁴J(PC) = 13 Hz] and 120 ppm [³J(PtC) = 75–81 Hz and ⁴J(PC) = 6 Hz] in the ¹³C-¹H NMR spectra.

The resonances near 116 ppm, with larger coupling constants, can be assigned to the trans cyano group to the phosphine ligand in **3a** and to the isocyanide ligand in **3c**. A similar geometric dependence of the chemical shifts of the cyano groups in the dicyanomethylene moiety has also been observed in 3-(dicyanomethylene)indol-2-one compounds¹⁵. The C-4 resonance of the C(CN)₂ group is highly shielded in the range of 49–71 ppm, probably due to a considerable amount of the negative charge residing on this carbon. Although these values are unusual, similar chemical shifts of carbons bearing the two nitrile groups have been observed in other organic^{15,16} and organometallic compounds¹⁷. Aromatic C-*ipso* (C-7 and C-8) resonances of the TRYA moiety in ¹³C-NMR spectra are the most deshielded signals and are easily differentiated by magnitudes of the platinum satellites. However, the conjugation effect of C-8 does not considerably alter the net amount of positive charge over the C₃ ring, owing to the small difference between the two signals. The assignments of the endocyclic carbons C-1, C-2 and C-3 to the resonances at a lower field in the NMR spectra are based upon the relative magnitudes of the ¹J(PtC) couplings. As observed at electronic η³-allylic structures, the signal of the central C-2

Table 1. Selected $^{13}\text{C}\{-^1\text{H}\}$ NMR data for quaternary carbons of platinacyclobutene complexes^a.

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
3a	158.7 (648)	168.5 (89)	163.5 (638)	70.6 (40)	120.7 (76)	116.0 (115)	141.0 (370)	136.4 (97)
			[109]	[10]	[6]	[13]	[4]	[3]
3b	160.5	170.3	167.7 [100]	48.6 (38)	120.6	116.3	143.2 (42)	136.5 (84)
3c	154.9 (630)	167.3 (84)	157.7 (677)	71.3 (38)	120.5 (81)	115.8 (117)	140.7 (29)	136.9 (99)
3d	155.0	167.2	156.7	71.4	119.3	116.7	139.4	134.3
e	146.3	166.4	153.3	39.4	116.2	116.2		

^aMeasured in CDCl_3 ; chemical shift (δ) in ppm relative to SiMe_4 ; $^{195}\text{Pt}\text{-}^{13}\text{C}$ and $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constants (Hz) are present in parentheses and in square brackets, respectively throughout table. Compounds: **3a**, $\text{L}_1 = \text{CNBu}^t$, $\text{L}_2 = \text{PPh}_3$; **3b**, $\text{L}_1 = \text{CNBu}^t$, $\text{L}_2 = \text{PCy}_3$; **3c**, $\text{L}_1 = \text{L}_2 = \text{CNBu}^t$; **3d**, $\text{L}_{12} = \text{COD}$; **e** = 1,2-dimethyl-3-dicyanomethylenecyclopropene¹⁶.

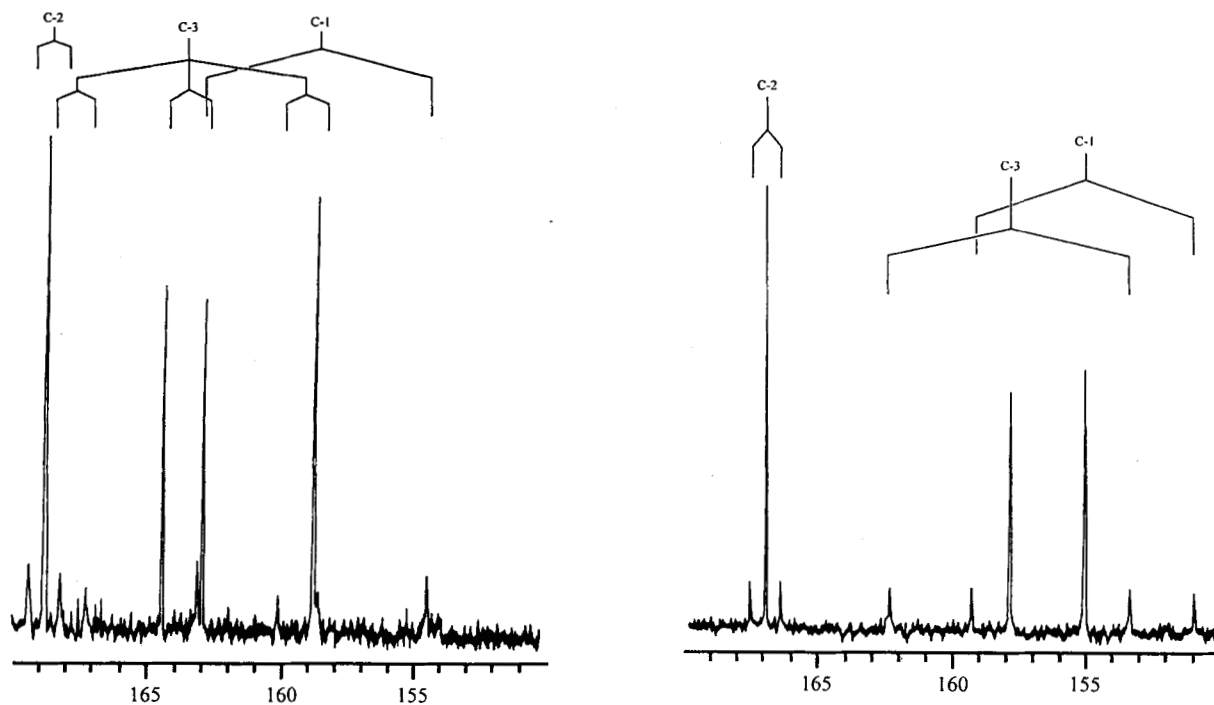


Figure 1. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra (75.5 MHz) of **3a** (top) and **3c** (bottom) between 150–170 ppm showing the resonances due to quaternary carbons of the PtTRYA ring.

invariably appears at the lowest field with a small $^1J(\text{PtC})$ (range 84–89 Hz). In contrast, C-1 and C-3 have large couplings in the range of 630–677 Hz, which are characteristic of carbon atoms s-bonded to platinum. Although the

chemical shift of C-1 is close to that of C-3 in the complex **3a**, the signal of C-3 is differentiated by a remarkably large $^2J(\text{PC})$ coupling of 109 Hz, probably due to the bulky triphenylphosphine ligand trans to the $\text{C}(\text{CN})_2$ group. A

single resonance in the $^3\text{P}\{-^1\text{H}\}$ NMR spectrum of **3a**, which has platinum satellites with a small $1J(\text{PtP})$ value of 2181 Hz, suggests a high trans influence of the $\text{C}(\text{CN})_2$ fragment. Moreover, the downfield shifts of the C_3 carbon resonances may be related to the increase in the trans influence of ligands L: $\text{COD} \approx \text{CNBu}^t < \text{PPh}_3 < \text{Pcy}_3$.

The contribution of the dipolar structure $\text{Pt}\{\text{Ph}_2\text{C}_3+\text{C}^-(\text{CN})_2\}$ to the resonance hybrid of $\text{Pt}\{\text{Ph}_2\text{C}_3=\text{C}(\text{CN})_2\}$ for **3a** to **3d** derivatives is now supported by ^{13}C -NMR data.

Conclusions

It was experimentally shown that TRYA can undergo two pathways in ring-opening reactions with platinum complexes $[\text{Pt}(\text{PR}_3)(\text{C}_2\text{H}_4)_2]$, $[\text{Pt}_3(\text{CNBu}^t)_6]$, and $\text{Pt}(\text{COD})_2$. The process of the activation of the three-membered ring apparently occurs through the initial formation of an η^2 complex, which may generate the carbene or dicarbene intermediates. An olefin complex has been previously isolated from the reaction between $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ and methylcyclopropenone at low temperature¹⁸.

Vinylcarbene complexes (1-metallabutadienes) have been invoked as intermediates in stoichiometric and catalytic metal-promoted reactions of cyclopropenes and in reactions of metal carbene with alkynes⁴. The insertions of the metal in either the carbon-carbon single or double bonds mainly depend on the nucleophilic nature of the ancillary ligands coordinated to platinum. Stronger donor fragments $\text{Pt}(\text{PR}_3)$ probably allow rapid conversion into a carbene complex, exclusively resulting in the formation of a platinumacyclobutene. However, the carbon-carbon double bond cleavage by $\text{Pt}(\text{Bu}^t\text{NC})_2$ fragments to form a dicarbene can be the result of a second attack of the other $\text{Pt}(\text{Bu}^t\text{NC})_2$ on the opposite side of the π complex, thereby populating the antibonding orbital of the C_3 system^{10,11}. The $\text{Pt}(\text{COD})$ fragment reacts with slightly less selectivity, and either platinumacyclobutene or propanediylidenediplatinum products are formed, depending on the ratios of the reactants.

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