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 [Pt\textsubscript{3}(CNBu\textsubscript{4})\textsubscript{6}] (nas razões molares de 2:1 e 1:1) e [Pt(COD)\textsubscript{2}] (na razão molar de 2:1), originando-se complexos propanodiilenodiplatina [Pt\textsubscript{2}(\textmu_{2}-(Ph)C)\textsubscript{2}C=\textsubscript{C}(CN)\textsubscript{2}](CNBu\textsubscript{4})\textsubscript{4} (1a) e [Pt\textsubscript{2}(\textmu_{2}-(Ph)C)\textsubscript{2}C=\textsubscript{C}(CN)\textsubscript{2}](COD)\textsubscript{2} (1b) (COD = 1,5-ciclooctadieno). No entanto, as reações de abertura anelar do TRYA com quantidades equimolares de [Pt(PR\textsubscript{3})(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}] (R = Ph, e Cy) conduzem à inserção da platina na ligação simples carbono-carbono, formando-se platinaclobutenos dinucleares [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}](2a, R = Ph e 2b, R = Cy). Os complexos 2a e 2b tratados com 2 e 4 equivalentes de CNBu\textsuperscript{4} dão os correspondentes complexos mononucleares [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(PR\textsubscript{3})(CNBu\textsubscript{4})] (3a, R = Ph e 3b, R = Cy) e [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(CNBu\textsubscript{4})\textsubscript{2}] (3c). A reação do [Pt(COD)\textsubscript{2}] com 1 equivalente do TRYA produz o platinaclobuteno [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(COD)] (3d). Além disso, os ligantes COD deslocam-se prontamente de 1b e 3d pela adição de um excesso de CNBu\textsuperscript{4}, fornecendo 1a e 3c.

The compound 1,2-diphenyl-3-(dicyanomethylene)cyclopropene (TRYA) undergoes carbon-carbon double bond cleavage in reactions with [Pt\textsubscript{3}(CNBu\textsubscript{4})\textsubscript{6}] (in 2:1 and 1:1 mol ratios) and [Pt(COD)\textsubscript{2}] (in 2:1 mol ratio), to give the propanediilenediplatinate complexes [Pt\textsubscript{2}(\textmu_{2}-(Ph)C)\textsubscript{2}C=\textsubscript{C}(CN)\textsubscript{2}](CNBu\textsubscript{4})\textsubscript{4} (1a) and [Pt\textsubscript{2}(\textmu_{2}-(Ph)C)\textsubscript{2}C=\textsubscript{C}(CN)\textsubscript{2}](COD)\textsubscript{2} (1b) (COD = 1,5-cyclooctadiene). However, ring-opening reactions of TRYA with equimolar amounts of [Pt(PR\textsubscript{3})(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}] (R = Ph, and Cy) lead to the insertion of the platinum into the single carbon-carbon bond, forming dinuclear platinacyclobutenes [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}] (2a, R = Ph and 2b, R = Cy). Complexes 2a and 2b, treated with 2 and 4 equivalents of CNBu\textsuperscript{4}, give the related mononuclear platinacyclobutenes [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)2(PR\textsubscript{3})(CNBu\textsubscript{4})] (3a, R = Ph and 3b, R = Cy) and [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(CNBu\textsubscript{4})\textsubscript{2}] (3c). The reaction of [Pt(COD)\textsubscript{2}] with 1 equivalent of TRYA produces the platinacyclobutene [PtC(Ph)=C(Ph)C=\textsubscript{C}(CN)\textsubscript{2}(COD)] (3d). Furthermore, the COD ligands are readily displaced from 1b and 3d by the addition of an excess of CNBu\textsuperscript{4}, 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 literature. Metallicacyclobutenes and bridged carbene complexes have been isolated either from ring-opening reactions of cyclopropenes, or indirectly from alkene-carbene complexes coupling at the metal. 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 C-3 atoms. Stoichiometric reactions of such methylenecyclopropanes 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 platinumacyclobutene rings. Cleavage reactions of the C=C link have only been observed in diphenylcyclopropane, accomplished by [Pt3(CNBu)6] and [Pt(COD)(mvk)] (mvk = methyl vinyl ketone), to give µ-2-oxo-1,3-diphenylpropanediylidene complexes [Pt2{µ2}(PhC)2CO}L4 (L = CNBu and L2 = COD), where the two PtL2 groups are bridged transversely by a perpendicular PhCC(O)CPh fragment. An interpretation of the emerging results was also the subject of a theoretical study.

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 platinumacyclobutenes 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 EP25 apparatus and are uncorrected. Molecular weight determinations in solution at three or more different concentrations were obtained on a Knauer Vapour-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, or 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 (H and C) and 85% phosphoric acid (P) 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 CNBu12 and TRYA13, and the complexes [Pt(COD)2], [Pt3(CNBu)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{µ2(PhC)2C=C(CN)2}(CNBu)4] (1a)

(i) TRYA (0.080 g, 0.315 mmol) was added to a stirred solution of [Pt3(CNBu)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 C35H34N6Pt2: 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 (CHC13), found: 988, calcd. 977. IR: ν(CN) at 2195 w, 2185 s and 2155 s cm⁻1. NMR: 1H (100.1 MHz), δ 7.62-2.72 (m, 10 H, Ph) and 1.40 (s, 36 H, Bu3); 13C{(1H) (25.2 MHz), δ 160.2 [s, C=C(CN)2], 44.0 (s, Ph, C=C=O), 129.9 (s, Ph, C6), 126.9 (s, CNBu), 125.5 (s, Ph, C=O), 124.4 (s, Ph, C6), 120.1 (s, C=C(CN)2 J(Ph) 16 Hz), 86.8 [C=C(CN)2], 80.4 [s, C2=C(CN)2, J(PhC) 552 Hz], 56.6 (s, C, Bu3), 29.2 (s, Bu3).

(ii) The reaction between TRYA (0.076 g, 0.30 mmol) and [Pt3(CNBu)6] (0.108 g, 0.10 mmol) was performed as described above to yield 1a (0.056 g 38%). Anal. Calcd. for C35H34N6Pt2: 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 (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{µ2(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 C35H34N6Pt2: C, 47.4; H, 4.0; N, 3.2.
Found: C, 46.7; H, 4.2; N, 2.8%. Mp 200 °C dec. IR; v(CN) at 2170 m and 2130 m cm⁻¹. NMR: ¹H (80 MHz), δ 7.60–6.68 (m, 10 H, Ph₃), 6.60–4.30 (m, 8 H, CH, COD, J(PtH) not discernible), and 2.90–2.00 (m, 16 H, CH₂, COD); ¹³C-¹H (25.2 MHz), δ 165.4 [s, C=C(CN)]₂, 139.6 (s, Ph, C₉H₈O), 128.5 (s, Ph, C₉), 128.4 (s, Ph, C₈), 127.9 (s, Ph, C₆), 117.6 [s, C=C(CN)]₂, 99.3 [C=C(CN)]₂, 97.2 [s, C₉=C(CN)]₂, J(PtH) not discernible, 95.5 [s, C=C, COD, J(PtC) 95 Hz], 93.6 [s, C=C, COD, J(PtH) 119 Hz], 31.0 (s, CH₂, COD), and 28.0 (s, CH₂, COD).

The preparation of dinuclear platinacyclobutene complexes

(a) [PtC(C(Pt)⁻=C(Pt)⁻=C(CN)]₂(PPH₃)] (2a)

[Pt(PPh₃)]₂(C₂H₄)] (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. C₁₁H₁₅N₃P₂Pt₂ requires C, 60.76; H, 3.54; N, 3.94%), m.p. 287–290 °C. Mol wt. (THF), found: 379, calc. 412/4 = 356. IR v(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) [Pt(C(CPh)(C(C(CN)]₂(C(CN)]₂) (2b)

[Pt(PCy₃)]₂(C₂H₄)] (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. C₁₂H₁₈N₃P₂Pt₂ requires C, 59.25; H, 5.94; N, 3.84%, m.p 267–275 °C. Mol wt. (trichloroethylene), found: 650, calc. 1460/2 = 730. IR v(CN) at 2227m and 2200 m cm⁻¹. NMR: ¹H (100.1 MHz, CDCl₃), δ 7.40–6.75 (m, 10 H, Ph), and 2.13–0.68 (m, 33 H, CH₂, Cy).

The preparation of mononuclear platinacyclobutene complexes

(a) [PtC(PPh₃)]₂(C(CN)]₂(PPh₃)] (3a)

CNBu ¹ (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 petroleum 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. C₁₁H₁₅N₃Pt₃ requires C, 61.95; H, 4.31; N, 5.29%, mp 176 °C. Mol wt. (CHCl₃), found: 824, calc. 794. IR v(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, Bu²), ¹¹C-¹H (75.7 MHz), δ 168.5 [d, C(PH), J(PtC) = 89 Hz], 163.5 [d, PtCC(CN)]₂, J(PtC) = 638 Hz, J(PtC) = 109 Hz], 158.7 [s, PtC(PH), J(PtC) = 647 Hz], 141.0 [d, Ph, TRYA, C₉H₈O, J(PtC) = 37 Hz, J(PtC) = 3 Hz], 136.4 [d, Ph, TRYA, J(PtC) = 97 Hz, J(PtC) = 3 Hz], 134.2–27.0 (Ph, PPH₃ and TRYA), 126.5 [s, CNBu ¹, J(PtC) = 1090 Hz], 120.7 [d, C(CCN)]₂, J(PtC) = 75 Hz, J(PtC) = 6 Hz], 116.0 [d, C(CCN)]₂, J(PtC) = 114 Hz, J(PtC) = 13 Hz], 70.6 [d, C(CCN)]₂, J(PtC) = 40 Hz, J(PtC) = 10 Hz], 58.1 (s, CNBu ¹), 29.1 (s, CH₃, Bu²), 31.3 [J(PtC) = 121.5 MHz], δ 16.31 [s, J(PtC) = 2181 Hz].

(b) [PtC(PPh₃)]₂(C(CCN)]₂(PPCy₃)] (3b)

CNBu ¹ (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. C₁₂H₁₅N₃Pt requires C, 60.56; H, 6.45; N, 5.17%). M.p 274 °C. Mol wt. (CHCl₃), found: 837, calc. 812. IR v(CN) at 2205s, 2200 w, and 2180 s cm⁻¹. NMR: ¹H (100 MHz), 7.27–6.80 (m, 10 H, Ph), 1.61 (s, 9 H, Bu²), and 2.13–0.68 (m, 33 H, CH₂, Cy); ¹¹C-¹H (25.2 MHz), δ 170.3 [s, C(PH)], 167.7 [d, PtCC(CN)]₂, J(PtC) = 100 Hz], 160.5 [s, PtC(PH)], IR v(CN) at 242 s, 2010 s cm⁻¹. ¹°C-¹H (18 Hz, J(PtC) = 42 Hz], 136.5 [s, Ph, C₉H₈O, J(PtC) = 84 Hz], 128.9–25.6 (Ph, TRYA), 120.6 and 116.3 [s, C(CCN)]₂, 58.5 [s, C, Bu²], 48.6 [s, C(CCN)]₂, 33.7 [d, CH₂, Cy, J(PtC) = 18 Hz, J(PtC) = 24 Hz], 29.8 [d, CH₂Cy, J(PtC) = 12 Hz], 29.7 (s, Bu²), 27.2 [d, CH₂Cy, J(PtC) = 11 Hz], and 26.1 (s, CH₂, Cy).

(c) [Pt(CPh)(C(CPh)]₂(C(CN)]₂(CNBu ⁴)] (3c)

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

CNBu ² (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. C₂₈H₂₅N₃Pt
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,
2120 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') and 1.45 (s, 9
H, Bu’); ¹³C–¹H (75.47 MHz), δ 167.3 [s, C(Ph)], ²(J(PPC)
= 84 Hz), 157.7 [s, Pt(CCCN)₂], ²(J(PPC) = 677 Hz), 154.9
[s, Pt(CPh)], ²(J(PPC) = 630 Hz), 140.7 [s, Ph, C̊₃p₉o₃], ²(J(PPC)
= 29], 136.9 [s, Ph, C̊₃p₉o₃, ²(J(PPC) = 99 Hz), 129.0–127.0
(Ph, TRYA), 128.4 [s, CNBu', ²(J(PPC) = 983 Hz), 120.5 [s,
C(CN)₂], ²(J(PPC) = 81 Hz), 115.8 [s, C(CN)₂], ²(J(PPC) = 117
Hz], 71.3 [s, C(CN)₂], ²(J(PPC) = 38 Hz], 58.1 [s, C, Bu’],
30.0 and 29.7 (s, CH₃, Bu’).

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

Complex 2a (0.200 g, 0.141 mmol) was added portion-
wise to a stirred solution of CNBu' (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 portion-
wise to a stirred solution of CNBut (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 3e (0.165
g, 95%). The IR and NMR data were identical to (i).

(d) [Pt(Ph)₃(C(Ph)C=C(CN)₂(CO))] (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-dichloro-
methane (50:50) to afford a pure sample of 3d (0.375 g,
90%). (Found: C, 55.38; H, 4.10; N, 5.06. C₂₆H₂₅N₂Pt
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], ²(J(PPH)
= 44 Hz], 5.30 [s, 2 H, CH, COD], ²(J(PPh) = 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, Pt(CCCN)₂], 155.0 [s, PtC(Ph)],
139.4 [s, Ph, C̊₃p₉o₃], ²(J(PPC) = 24 Hz], 134.3 [s, Ph, C̊₃p₉o₃,
²(J(PPC) = 113 Hz], 130–126 (Ph, TRYA), 119.3 and 116.7
[s, C(CN)₂], 103.9 [s, CH, COD, ²(J(PPC) = 64 Hz], 103.8
[s, CH, COD, ²(J(PPC) = 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(µ₂–(Ph)C)C=C(CN)₂]
(CNBu')₂ (1a) was selectively prepared by reacting a THF
solution of the cluster [Pt₂(CNBu')₂] with TRYA in 1:2 and
1:1 molar ratios, or by reaction of [Pt₂(µ₂–
(Ph)C)C=C(CN)₂(COD)] (1b) with an excess of CNBu'.
The formation of complex 1b depends on the reactant
ratios, requiring 2 equivalents of [Pt(COD)₂]. Otherwise,
the product will be the platincyanocyanobutene 3d. The
dinuclear [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)₂(C₂H₄)] (R = Cy and Ph) with TRYA in THF
solutions. They are good starting materials for the prepara-
tion of mononuclear platincyanocynobutenes 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' in THF
they gave [PtC(Ph)=C(Ph)C=C(CN)₂(PPh₃)(CNBu')₂] (3a)
and [PtC(Ph)=C(Ph)C=C(CN)₂(PC₃Y₃)(CNBu')₂] (3b), re-
spectively. 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')₂] (3c). The related com-
plex [PtC(Ph)=C(Ph)C=C(CN)₂(COD)] (3d) is straightfor-
wardly prepared by reacting [Pt(COD)₂] with 1 equiva-
lent of TRYA. Additional evidence for the formul-
ation of 3d is the formation of 3e through the ready
replacement of the COD ligand by two CNBu'. The chem-
istry is summarized in the Scheme 1.

All complexes are stable in air in the solid state. Mo-
olecular weight measurements of dinuclear complexes show
the dissociation of 2b into two fragments in trichlo-
roethylen, 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 car-
ried out in THF only, the dinuclear complex was ob-
tained.⁸ 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 2-oxo-
1,3-diphenylpropanediylidene [Pt₂(µ₂–(Ph)C)C=CO]₄₉₁₀.
The ¹H-NMR spectrum of 1a displays characteristic signals
of the phenyl protons in the range of 7.63–7.23 ppm, and a
single sharp resonance of the Bu 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-¹¹H NMR data for the platinacyclobutene. The assignment of the quaternary carbons of the PtTRYA unit was mainly based on the 195Pt-¹³C and ¹³P-¹³C spin coupling patterns of the more soluble 2a and 3c.

All the platinacyclobutene monomers show two sets of chemical shifts for C-6 and C-5 around 116 [¹J(PtC) = 114–117 Hz and ²J(PC) = 13 Hz] and 120 ppm [¹J(PtC) = 75–81 Hz and ²J(PC) = 6 Hz] in the ¹³C-¹¹H 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 compounds.¹³ 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 organic¹⁵,¹⁶ and organometallic compounds.¹⁷ 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 η²-allylic structures, the signal of the central C-2
Table 1. Selected $^{13}$C-$^1$H NMR data for quaternary carbons of platinacyclobutene complexes$^a$.

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

$^a$ Measured in CDCl$_3$; chemical shift (δ) in ppm relative to SiMe$_4$; $^{155}$Pt-$^{13}$C and $^{31}$P-$^{13}$C coupling constants (Hz) are present in parentheses and in square brackets, respectively throughout table. Compounds: 3a, $L_1 = CNBu^+$; $L_2 = PPh_3$; 3b, $L_1 = CNBu^+$; $L_2 = PCy_3$; 3c, $L_1 = L_2 = CNBu^+$; 3d, $L_1 = COD$; e = 1,2-dimethyl-3-dicyanomethylene cyclopropane.$^{16}$

Figure 1. $^{13}$C-$^1$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 Pt(II) ring.

invariably appears at the lowest field with a small $^1J$(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 $^2J$(PC) coupling of 109 Hz, probably due to the bulky triphenylphosphine ligand trans to the C(CN)$_2$ group. A
single resonance in the $^{31}$P-$^{1}$H NMR spectrum of 3a, which has platinum satellites with a small 1J(PP) value of 2181 Hz, suggests a high trans influence of the C(CN)₂ fragment. Moreover, the downfield shifts of the C₃ carbon resonances may be related to the increase in the trans influence of ligands L: COD ≈ CNBu⁺<PPh₃<PCy₃.

The contribution of the dipolar structure Pt{Ph₂C₆+<C(CN)₂} to the resonance hybrid of Pt{Ph₂C₆=C(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 [Pt(PR₃)(C₂H₄)₂], [[Pt₃(CNBu)₆], and Pt(COD)₂]. The process of the formation of the three-membered ring apparently occurs through the initial formation of an η² complex, which may generate the carbene or dicarbene intermediates. An olefin complex has been previously isolated from the reaction between [Pt(PPh₃)₂(C₂H₄)] and methylcyclopentene at low temperature.

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 alkynes. 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 Pt(PR₃) probably allow rapid conversion into a carbene complex, exclusively resulting in the formation of a platinumacyclobutene. However, the carbon-carbon double bond cleavage by Pt(Bu¹NC)₂ fragments to form a dicarbene can be the result of a second attack of the other Pt(Bu¹NC)₂ on the opposite side of the π complex, thereby populating the antibonding orbital of the C₃ system. The Pt(COD) fragment reacts with slightly less selectivity, and either platinumacyclobutene or propanediyldenediplatinum products are formed, depending on the ratios of the reactants.

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References


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