Synthesis and Molecular Structure of 1,2-Diphenyl-3-Platina-4-dicyanomethylene-cyclobutene Derivatives

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Reactions of zero-valent complexes of platinum and palladium with electronegatively activated three- [1] or four- [2] membered carbocycles give ring opening reactions with insertion of the metal in the carbon–carbon bond. It has been proposed that the driving force in these reactions is the amount of positive charge on the carbon atom, rather than the strain energy of the ring [2]. Platinum(0) and palladium(0) complexes react in a similar fashion with diphenylcyclopropenone [3] and cyclobutenedione [4] derivatives. With these systems, however, metal–olefin intermediates have been isolated depending upon the conditions [4, 5].

In order to compare the two models of reactions, (i) ring opening or (ii) formation of metal–olefin compounds, we have investigated the reactivity of $[(PPh_3)_2Pt(C_2H_4)]$, **I**, with 1,2-diphenyl-3-dicyanomethylenecyclopropene [6] **II** (hereafter Trya), where stable metal–olefin complexes could be obtained [7].
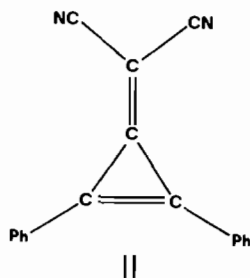
Reaction of **I** and **II** in refluxing benzene for 1 hr followed by crystallisation from the same solvent or from a benzene–methanol mixture gave two different crystalline products, **III** and **IV**. The i.r. spectra in nujol mull, in the $\nu(CN)$ region, showed one band at 2220 cm^{-1} for **III** and two bands at 2210 and 2245 cm^{-1} for **IV**. The complete characterisation of the two compounds was achieved through X-ray analysis.

Crystal Data

III, $a = 10.110(5)$, $b = 19.47(1)$, $c = 23.16(1)$ Å, $\beta = 99.1(1)°$, $D_c = 1.44$, $Z = 4[(Ph_3P)_2Pt\ Trya]$,

$\mu(MoK\alpha) = 34$ cm^{-1}, space group $P2_1/n$. **IV**, $a = 15.491(7)$, $b = 21.04(1)$, $c = 10.899(5)$ Å, $\beta = 100.7(1)°$, $D_s = 1.53$, $D_c = 1.50$, $Z = 4$ $[(Ph_3PPtTrya)_2 \cdot 2C_6H_6]$. $\mu(MoK\alpha) = 43$ cm^{-1}, space group $P2_1/n$. A total of 1080 (**III**) and 2577 (**IV**) independent reflexions, having $I > 3\sigma(I)$, were measured on a Siemens automated diffractometer, using MoKα radiation (θ max $\leqslant 24°$). Correction for Lorentz and polarization factors was applied. The structures were solved by Patterson and Fourier methods and the block-diagonal least-squares refinement reached R = 0.054 (**III**) and 0.075 (**IV**).
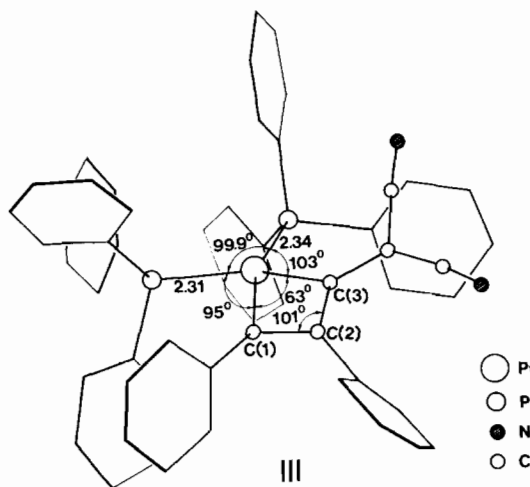

Figure 1. A sketch of the monomeric species **III**. E.s.d.'s are 0.01 Å for bond lengths and 0.4–1° for bond angles involving Pt.
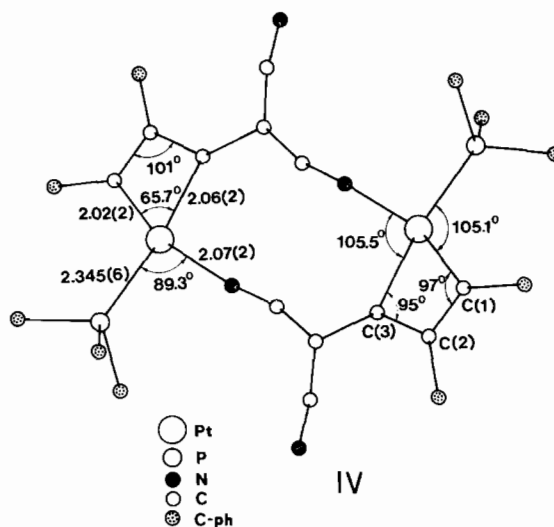

Figure 2. A sketch of the centrosymmetric dimeric species **IV**. For clarity only the first carbon atom of the phenyl groups is drawn. E.s.d.'s are 0.6° and 1–2° for angles involving Pt and other atoms, respectively.

The structures of **III** and **IV** are shown in Figures 1 and 2 where some bond lengths and angles are given. The X-ray analysis results of both complexes show that a ring opening reaction has occurred probably via a nucleophilic attack of the $Pt(PPh_3)_2$ moiety to the carbon atom bearing the larger positive charge [1, 2]. It is worthy of note that the puckering angle of the platinacycle (*i.e.* the angle between C(1)–Pt–C(3) and C(1)–C(2)–C(3) platines) is greater in **III** ($23°$) than in **IV** ($9°$) as well as the dihedral angle between the planes of the $=C(CN)_2$ and C(1)–C(2)–C(3) groups ($28°$ in **III**; $10°$ in **IV**). The larger distortion of **III** may be easily interpreted on the basis of greater steric hindrance exerted by one phosphine ligand on the $=C(CN)_2$ group. In fact, in the absence of steric effects we should expect that there should be no significant distortion in the platinacycle in view of the ligand nature. The above results suggest that **III** could release a phosphine ligand yielding a less strained dimeric species like **IV**. Thus in refluxing THF, **III** is completely converted to **IV**, which after addition of an excess of PPh_3 restores **III**. These results show the existence in solution of the equilibrium $2III \rightleftarrows IV + 2PPh_3$, which depends however on the solvent used, **III** being destabilized in coordinating solvents.

Acknowledgments

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