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Preliminary communication

Carbon–carbon bond rupture promoted by palladium(0) and platinum(0) triphenylphosphine complexes

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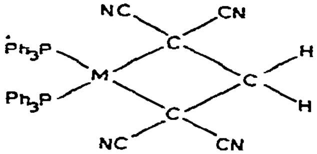
SUMMARY

Treatment of $M(PPh_3)_4$ with 1,1,2,2-tetracyanocyclopropane gives (I), where M = Pt or Pd, and with M = Pt treatment with tetracyanoethylene oxide gives (II), produced by cleavage of the C–C bond.

Catalytic isomerization of highly strained ring systems such as bicyclo[1.1.0]-butanes or bicyclo[2.1.0]pentanes proceeds under mild conditions in the presence of transition metal complexes. Two mechanistic schemes have been proposed for skeletal rearrangements of bicyclo[1.1.0]butane derivatives; these involve either the formation of a metal–carbene intermediate[1] or that of a metal-stabilized carbonium ion, as in the case of the isomerization of bicyclopropane catalysed by silver ion[2]. (A similar cationic intermediate has been proposed also for the reaction of acetylenes with *trans*-$[PtL_2(CH_3)Cl]$ [3].) The initial step in the skeletal rearrangements of the named carbocycles is the cleavage of the carbon–carbon bond, the reaction products depending on the nature of both the metal and the substituent groups.

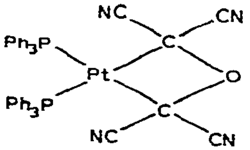
We have studied the ring opening of a cyclopropane derivative by tetrakis-(triphenylphosphine)-platinum(0) and -palladium(0), with a view to isolating complexes analogous to the intermediates thought to be involved in the isomerization of strained carbocycles. The organic substrates used were 1,1,2,2-tetracyanocyclopropane[4] (TCCP) and tetracyanoethylene oxide[5] (TCNEO).

Reactions with 1,1,2,2-tetracyanocyclopropane (TCCP). Treatment of $[M(PPh_3)_4]$ in THF with TCCP under N_2 at room temperature for half an hour followed by addition of methanol gave a white solid (m.p. 220°–255° for M = Pt and 170°–173° for M = Pd) which analyzed as $M(PPh_3)_2C_3H_2(CN)_4$ (Molecular weights in chloroform: calcd. 862; found 795 (M = Pt); calcd. 773; found 725 (M = Pd)). The ^1H NMR spectra in $CDCl_3$ showed absorptions of the methylene protons at τ 8.36 (singlet) for the platinum derivative, and at τ 8.40 (singlet) for the corresponding palladium product. The infrared spectra of the reaction products show one strong sharp band in the solid (Nujol mull) and also in solution ($CHCl_3$) at 2220 (M = Pt) and 2200 cm^{-1} (M = Pd), attributable to the CN stretching frequency. The ^1H NMR and IR spectra are fairly similar to those of the parent organic ligand, 1,1,2,2-tetracyanocyclopropane (methylene protons at τ 8.08 and ν(CN) at 2265 cm^{-1})[4]. Thus we formulate the products as (I). Such a metallocyclobutane ring system has been identified previously for Pt^{IV} [6].



(I)

Reactions with tetracyanoethylene oxide. Similar treatment of $[Pt(PPh_3)_4]$ with tetracyanoethylene oxide gave a white product (m.p. 210°–215°) which analyzed as $Pt(PPh_3)_2C_2(CN)_4O$. Its molecular weight in $CHCl_3$ is 796 (calcd. 864). The IR spectrum showed a strong absorption band at 2220 cm^{-1} ($CHCl_3$ or Nujol mull) assigned to the CN stretching frequency, and a band at 1070 cm^{-1} attributed to ν(C–O–C). By comparison of the spectroscopic properties with those of (I), the complex is assigned structure (II).



(II)

This unprecedented mode of ring opening of an olefin oxide may represent a general reaction of negatively-substituted small rings containing heteroatoms. If so these reactions would provide a useful synthetic route to various metallocyclic systems containing metal–carbon σ-bonds*.

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*The compound $(PPh_3)_2Pt(TCNEO)$ has been prepared independently by W.H. Baddley and W.D. Pitts (personal communication).