Intramolecular Cyclization of π-1-Chloro-3-phenylallylpalladium(II) Complexes. A Novel Route to Stable Indenyl Complexes of Palladium(II)

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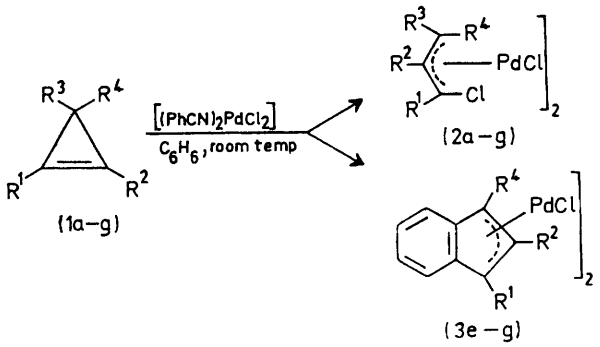
Summary Intramolecular cyclization of the π-allylpalladium(II) complexes derived from the reaction of [$(PhCN)_2PdCl_2$] with tri- and tetra-substituted cyclopropenes affords novel indenylpalladium(II) complexes with and without strong donor ligand activation.

WE have previously shown that the reaction of [$(PhCN)_2PdCl_2$] with the cyclopropenes (**1a**)[1] and (**1b**—**d**)[2] proceeds with quantitative formation of the corresponding π-allyl complexes (**2a**—**d**). We now report that under identical conditions the tetrasubstituted cyclopropenes (**1e**—**g**) unexpectedly afford the stable indenyl complexes (**3e**—**g**) with concomitant HCl evolution. Mechanistic considerations indicate that these novel indenyl complexes most likely arise from spontaneous intramolecular cyclization of the intermediate π-allylic complexes (**2e**—**g**).

The crude indenyl complex (**3e**), obtained in 40—60% yield from reaction of (**1e**) with [$(PhCN)_2PdCl_2$] in benzene

at room temperature, was chromatographed on silica gel and repeatedly recrystallized from benzene–hexane (1 : 1) to give a grey-green solid, m.p. 151—153 °C, analysing most nearly for $C_{44}H_{34}Cl_2Pd$ [ν_{KBr} 565 and 545 cm^{-1}; δ (C_6D_6) 7·6—7·2 (5H, m), 7·1—6·8 (5H, m), 6·72 (4H, s), and 1·01 (3H, s)]. Treatment of (**3e**) with aqueous KCN gave a quantitative yield of a mixture (87 : 13) of 3-methyl-1,2-diphenyl- and 1-methyl-2,3-diphenylindene[3] (n.m.r. comparison with authentic samples[4]).

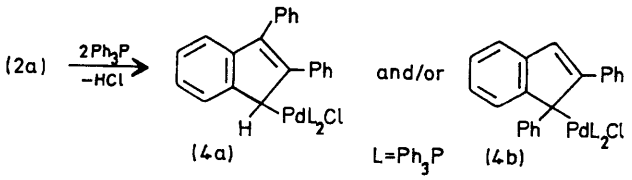


a; $R^1 = R^2 = R^3 = Ph$, $R^4 = H$
b; $R^1 = R^2 = Ph$, $R^3 = R^4 = Me$
c; $R^1 = Ph$, $R^2 = R^3 = R^4 = Me$
d; $R^1 = R^2 = R^3 = Me$, $R^4 = Ph$
e; $R^1 = R^2 = R^3 = Ph$, $R^4 = Me$
f; $R^1 = R^4 = Me$, $R^2 = R^3 = Ph$
g; $R^1 = R^2 = R^3 = R^4 = Ph$

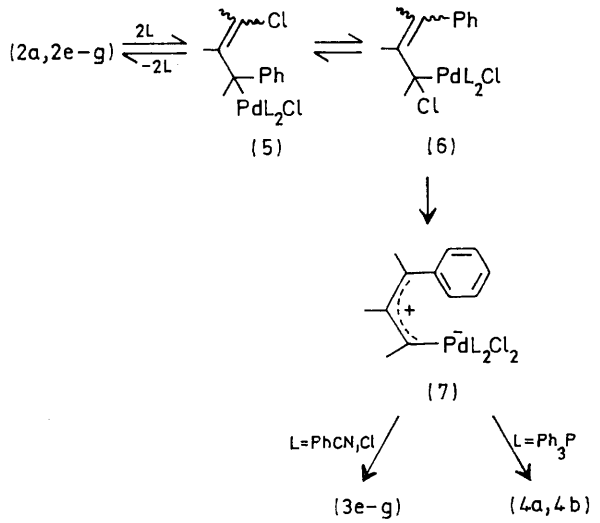
Chromatography and repeated recrystallization of the similarly isolated indenyl complexes (**3f**) and (**3g**) gave material with analytical data high in chlorine, although the i.r. spectra again showed strong absorptions at 565 and 545 cm^{-1}. More importantly, treatment of (**3f**) with aqueous KCN gave a single product identified as 1,3-dimethyl-2-phenylindene,† m.p. 73—74 °C; δ ($CDCl_3$) 7·3—6·9 (9H, m), 3·75 (1H, q, J 7·5 Hz), 2·20 (3H, d, J 2·0 Hz), and 1·15 (3H, d, J 7·5 Hz). Similar treatment of (**3g**) with aqueous KCN gave 1,2,3-triphenylindene[5] as the sole product in agreement with the assigned structure.

The probable mechanism of the Pd-promoted rearrangement of the cyclopropenes (**1e**—**g**) to the indenyl complexes (**3e**—**g**) was investigated by the reaction of the π-allyl complex (**2a**) with PPh_3. It was found that 2 equiv. of the phosphine smoothly converted (**2a**) into the σ-indenyl complexes (**4a**) and/or (**4b**),† with HCl evolution, in 91% isolated yield; m.p. 210—220 °C(decomp); λ_{max} (log ϵ) (CH_2Cl_2) 232 (4·92), 290 (3·92), and 315sh (2·11) nm; ν_{Pd-Cl} (CsI and Nujol) 295 and 285 cm^{-1}; δ ($CDCl_3$) 8·0—7·0 (m). Reduction of (**4**) with $LiAlH_4$ gave a mixture of 1,2- and 2,3-diphenylindene[6] in agreement with the proposed structure.‡

The PPh_3-induced conversion of (**2a**) into the indenylpalladium(II) complex (**4**) clearly implicates the intermediacy of the π-allyl complexes (**2e**—**g**) in the similar Pd-promoted conversions of (**1e**—**g**) into (**3e**—**g**). The



Scheme shows a mechanism that is consistent with the ready intramolecular cyclization of 1-chloro-3-phenyl-π-allylpalladium(II) chloride complexes. Ample precedent exists for the initial step of this mechanism, a ligand-assisted π- to σ-allyl interconversion.[7] The subsequent formation and internal cyclization of the postulated σ-palladium allylic cation (**7**) provides an attractive explanation for the facility of these organopalladium transformations that is consistent with the expected ability of palladium greatly to activate the chloride in (**6**) to ionization. Although cationic metal complexes related to (**7**) have been previously postulated, their potential importance to Pd- and Pt-mediated reactions has been largely ignored.§



SCHEME

In view of the fact that strong donor ligands such as PPh_3 were not required to initiate indenyl complex formation from (**2e**—**g**) one may conclude that enhanced steric crowding associated with the terminal substituents of these allylic complexes promotes ready weak-ligand-assisted interconversion with the less constrained σ-complexes (**5**)

† All new compounds gave satisfactory elemental analyses unless otherwise noted.

‡ A separate experiment using PMe_2Ph established (n.m.r.) the *trans* orientation of the phosphine ligands in the σ-indenyl complex (**4**; L = $PhPMe_2$). See P. Mushak, Ph.D. Dissertation, University of Florida, 1970, for further details regarding the structure of (**4**).

§ A previously postulated homoallylic counterpart to the allylic ion (**7**) (H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2285) is a notable exception.

and (**6**; L = PhCN, Cl), which then triggers the ionization–cyclization sequence. Of the isolated π-allyl complexes (**2b—d**) derived from tetrasubstituted cyclopropenes, only (**2d**) has the requisite phenyl substituent at R^3 (or R^4) for internal cyclization. In line with the above observations (**2d**) was found to have limited stability when stored and to decompose rapidly with evolution of HCl on moderate heating.

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