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Preliminary communication

INTERACTIONS OF SMALL ORGANIC RINGS WITH TRANSITION METALS; AN UNUSUAL 1,3-CHLOROPALLADATION OF ALKYLMETHYLENECYCLOPROPANES

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Summary

Methylenecyclopropanes bearing alkyl substituents on the cyclopropane ring are shown to undergo addition of the elements of Pd—Cl in an unambiguous 1,3-fashion, in contrast to their unsubstituted parent. A mechanism involving a dipolar transition state is proposed.

The organic chemistry of palladium(II) is replete with examples of chloropalladation reactions, in which the elements of Pd—Cl add to unsaturated hydrocarbons in a 1,2-fashion [1]. Such additions are known to occur with both *cis*- [2] and *trans*-stereochemistries [3]. The recent interest in the transition metal catalyzed oligomerizations and cooligomerizations of methylenecyclopropanes, in which cleavage of the cyclopropane moiety can occur along either one of the two possible edges of the ring [4], prompts us to report our results concerning a possible model for such systems. We here report that chloropalladation of methylenecyclopropanes bearing alkyl ring substituents occurs by a unique 1,3-addition of the elements of Pd—Cl.

Reactions of unsubstituted [5], and methoxycarbonyl-substituted [6,7], methylenecyclopropanes (Ia—Ic) with $Pd(MeCN)_2Cl_2$ in dichloromethane or benzene solution have been shown to afford ultimately the η^3-allyl complexes IIa and IIb. The key step in this ring-opening process was shown [6] to involve 1,2-chloropalladation of the olefin function, the chloride migrating to the internal carbon center, followed by cleavage of the 1,2-bond of the cyclopropane ring and a subsequent metal-promoted H-shift [7]. Under identical conditions, however, 2,2-diphenylmethylenecyclopropane (Id) has been shown to afford only complex III in an alternative reaction mode involving rupture of the 2,3 σ-bond of the cyclopropane ring [5]. We anticipated that formation of III

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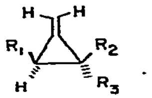
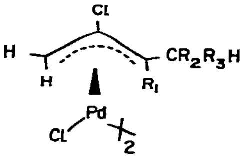
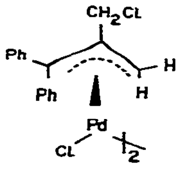


Ia. $R_1 = R_2 = R_3 = H$.
Ib. $R_1 = R_2 = CO_2Me$; $R_3 = H$.
Ic. $R_1 = R_3 = CO_2Me$; $R_2 = H$.
Id. $R_1 = H$; $R_2 = R_3 = Ph$.
Ie. $R_1 = R_2 = Me$; $R_3 = H$.
If. $R_1 = R_3 = Me$; $R_2 = H$.
Ig. $R_1, R_2 = -(CH_2)_4-$; $R_3 = H$.
Ih. $R_1 = H$; $R_2 = R_3 = Me$.



IIa $R_1 = R_2 = R_3 = H$.
IIb $R_1 = R_2 = CO_2Me$; $R_3 = H$.



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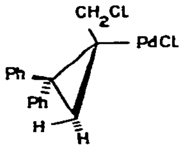

(IV)

might occur via initial 1,2-chloropalladation of the olefinic function of Id, in the opposite sense, to generate the cyclopropylpalladium intermediate IV, which could then undergo a spontaneous ring-opening to give the observed product. Similar ring-openings of cyclopropylplatinum species have been recently reported [8]. We therefore sought to test this postulate by examining suitably substituted systems.

Reaction of either *cis*-2,3-dimethylmethylenecyclopropane (Ie) [9] or *trans*-2,3-dimethylmethylenecyclopropane (If) [9] with $Pd(MeCN)_2Cl_2$ (CH_2Cl_2 solution; 20°C) was complete in seconds to afford quantitatively the same η^3-allyl complex (V), derived from cleavage of the 2,3 σ-bond of the cyclopropane ring. Complex V exists, in $CDCl_3$ solution, as a 3.3/1.0 mixture of two diastereoisomeric pairs of enantiomers, the chiral substituent at C(2) inducing a preferential coordination of Pd to one enantiotopic face of the allyl fragment*. Under

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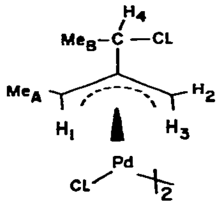
[*] ^{1}H NMR unambiguously defines the structures of all reported compounds. Satisfactory microanalyses have been obtained in all cases. The presence of the mixture of diastereoisomers of V is evidenced by duplication of all the resonances: ^{1}H NMR (δ, ppm; J, Hz) of major component (270 MHz; $CDCl_3$), δ 4.88 (q, J 6.6, H(4)), 3.96 (s, H(2)), 3.76 (q, J 6.6, H(1)), 2.64 (s, H(3)), 1.80 (d, J 6.6, Me_B), 1.32 (d, J 6.6, Me_A); ^{1}H NMR of minor component (270 MHz; $CDCl_3$), δ 4.88 (q, J 6.6, H(4)), 4.18 (s, H(2)), 3.74 (q, J 6.6, H(1)), 2.57 (s, H(3)), 1.70 (d, J 6.6, Me_B), 1.30 (d, J 6.6, Me_A). Complex VI exists in solution as only one of a possible pair of diastereoisomers; no duplication of ^{1}H NMR resonances is observed: ^{1}H NMR (270 MHz; $CDCl_3$), δ 4.68 (dd, J' s 5.5, 1.5, H(4)), 3.87 (dd, J' s 6, 1, H(1)), 3.78 (s, H(2)), 2.83 (s, H(3)), 2.5—1.2 (m, aliphatic ring protons). Complex VII: ^{1}H NMR (270 MHz; $CDCl_3$), δ 4.18 (s, H(1)), 2.83 (s, H(2)), 1.89 (s, Me). Complex VIII: ^{1}H NMR (270 MHz; $CDCl_3$), δ 4.43 (d, J 12, H(3)), 3.91 (d, J 12, H(4)), 3.81 (s, H(1)), 3.26 (s, H(2)), 1.46 (s, Me_A), 1.32 (s, Me_B).



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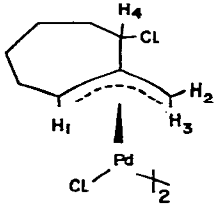

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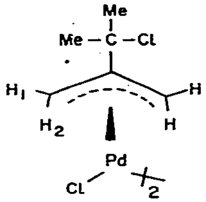

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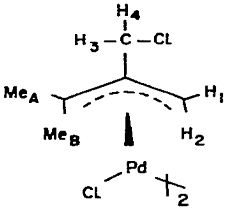

(VIII)

(IX)

identical conditions 7-methylenenorcarane (Ig) [9] afforded VI in quantitative yield. Similar reaction of 2,2-dimethylmethylenecyclopropane (Ih) [9] gave a quantitative yield of a 9/1 mixture of VII and VIII. Recrystallisation from CH_2Cl_2/hexane afforded pure VII, which did not rearrange to VIII in refluxing benzene; the original product mixture must be the result of kinetic selectivity. Similar complexes V and VI showed no proclivity for thermal rearrangement under conditions far more rigorous than those of their genesis. Notably, isopropylidenecyclopropane (IX) was not chloropalladated under these conditions, only starting materials could be recovered after 1 h in refluxing benzene.

Clearly, these results cannot be reconciled with the intermediacy of a cyclopropylpalladium species IV. A metallocyclobutane intermediate [4], resulting from direct oxidative insertion of palladium into the cyclopropane ring, also seems unlikely, since steric hindrance at the olefinic function, as in IX, suppresses the reaction*. Therefore chloropalladation must be initiated by attack of the metal at the olefinic site. We propose that the transition state for chloropalladation is dipolar in nature, represented by the extreme zwitterionic structure X. In cases where the ring substituents are H or CO_2Me (Ia–Ic) a simple

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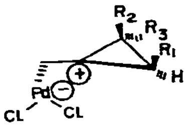
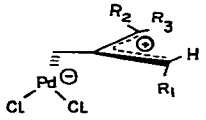
*Such an oxidative insertion pathway must be considered in view of the ready reactions of platinum(II) with cyclopropanes [10].

1,2-chloropalladation then occurs [6]; in cases where the ring substituents are more capable of stabilizing a positive charge build-up (Me or Ph; Id—Ih) extensive ring-opening occurs in the transition state [11]. An extreme version is depicted as XI. Intramolecular trapping of the resultant allylic cation by chloride results in a net 1,3-chloropalladation reaction. The kinetic selectivity in forming VII in preference to VIII in the chloropalladation of Ih further supports this hypothesis [12,13], and is highly reminiscent of the reactions of Ih with $Pb(OAc)_4$ [14] and with $Hg(OAc)_2$ [15].



(X)



(XI)

Ring-openings of cyclopropyl cations are constrained to occur in a disrotatory fashion [11,16]; the transition states for the chloropalladation of Ie and If should be geometrically different and might be expected to lead to different geometric isomers of V, a feature which is not observed*. A rapid $\eta^3 \to \eta^1 \to \eta^3$ transformation of the η^3-allylic fragment occurring subsequent to, and faster than, the chloropalladation step would serve to equilibrate such geometrical isomers [17]. That this is indeed the case is demonstrated by low temperature NMR monitoring of the chloropalladation of either Ie or If; only resonances due to the equilibrium mixture of diastereoisomers of V are ever observed. This can be reconciled by rapid $\eta^3 \to \eta^1 \to \eta^3$ transformations since equilibration of diastereoisomeric pairs of enantiomers requires movement of Pd from one enantiotopic face of the allyl ligand to the other.

In light of our results the previously reported chloropalladation of Id to give only III [5] remains an anomaly; one might expect preferential migration of Cl to the phenyl substituted ring carbon [13]. Experiments designed to elucidate this anomaly, and to explore further the nature of the trimethylenemethane-like species XI are in progress.

Our results demonstrate the first characterized instances of 1,3-chloropalladation and strongly infer a dipolar transition state for this process. Dipolar transition states for carbopalladation reactions have been previously suggested [18]. Perhaps the most remarkable feature of this work is the absolute difference in reaction mode (1,2- vs. 1,3-chloropalladation) observed merely by substituting Me for H on the cyclopropane ring.

Acknowledgement

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*Comparison of ^{1}H NMR data for V and VI clearly defines the position of Me_A in V as being *syn*; the chemical shifts of H(1) in VI, which is constrained to be *anti*, and H(1) in V are almost identical.

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