Transition-metal Complexes of Methylenecyclopropanes: Ring-opening Reactions Promoted by Palladium(II)

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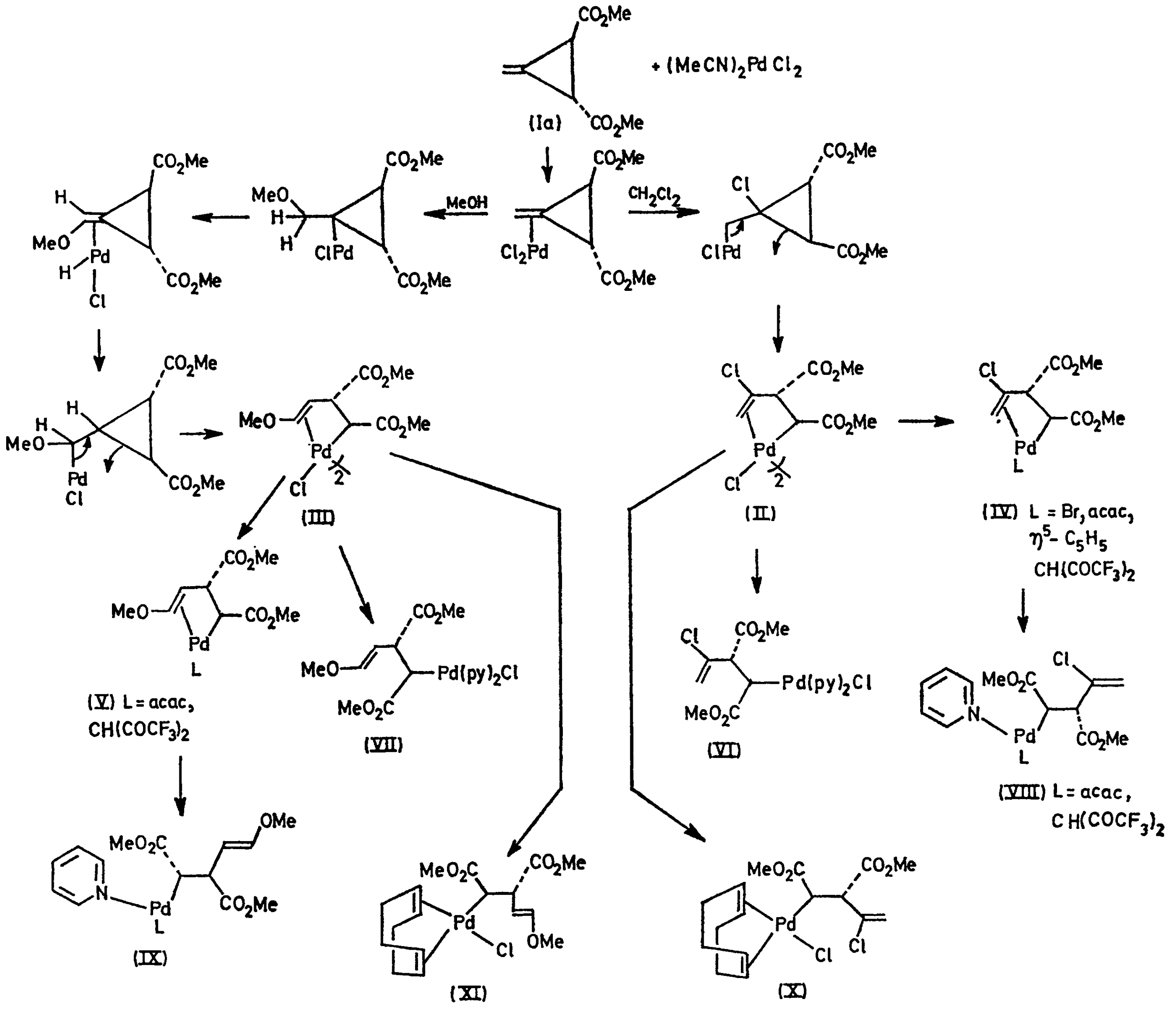
Summary A variety of stable 1,2-η-bonded methylene cyclopropane complexes of Rh^{I}, Ir^{I}, Pt^{0}, and Pt^{II} are reported; isomers of Feist's acid dimethyl ester react with $PdCl_2(MeCN)_2$ to yield 1,3-enyl complexes of palladium(II); stable alkyl complexes of Pd^{II} containing β-hydrogen atoms are reported, and their stability is discussed.

Transition metal promoted reactions of methylenecyclopropanes have aroused considerable interest, particularly as to the role of the metal in promoting the opening of the cyclopropane ring.[1,2] Intermediate 1,2-η-bonded methylenecyclopropane complexes have been implicated in the Ni^{0}-catalysed oligomerisation and codimerisation reactions of methylenecyclopropane.[1] Reactions of the *trans*- and *cis*-isomers of Feist's acid dimethyl ester (Ia) and (Ib) with $Fe_2(CO)_9$ initially yield (olefin)$Fe(CO)_4$ complexes, which thermally decompose to give (1,3-diene)$Fe(CO)_3$ species.[3] Methylenecyclopropane and 2,2-diphenylmethylenecyclopropane react with $(PhCN)_2PdCl_2$ to give π-allylic complexes of palladium(II).[4]

We now report that stable 1,2-η-bonded methylenecyclopropane complexes of Rh^{I}, Ir^{I}, Pt^{0}, and Pt^{II} can readily be prepared. Treatment of the appropriate π-ethylene metal complex with methylenecyclopropane, (Ia), or (Ib), displaces ethylene and yields (un)$_2$ML [M = Rh; un = methylenecyclopropane, (Ia), (Ib); L = Cl, acac, η^5-C_5H_5: M = Ir; L = acac; un = (Ia)], (un)$Pt(PPh_3)_2$ [un = methylenecyclopropane, (Ia), (Ib)], and *trans*-(un)$PtCl_2$(pyridine) [un = (Ia), (Ib)]. A crystallographic determination has shown that the geometry of co-ordinated methylenecyclo-



Scheme

propane in acetylacetonatobis(methylenecyclopropane)-rhodium(I) closely resembles that of co-ordinated 1,2-dienes.[5] Oxidative insertion of low valent metals into the cyclopropane ring of the above complexes is not a readily available reaction pathway. The cyclopropane ring in the Pt^0 and Pt^{II} complexes of (Ia) remains intact at 80°, although Pt^0 [6] and Pt^{II} [7] have been shown to insert into the σ-bonds of cyclopropanes.

In contrast, reaction of (Ia) and $(MeCN)_2PdCl_2$, or $[(C_2H_4)PdCl_2]_2$, in CH_2Cl_2 at 20°, does not yield a simple olefin complex, but produces the ring-opened complex (II) in high yield. Changing the reaction solvent to MeOH alters the stereochemical course of the reaction to give (III), to the complete exclusion of (II). Analogous isomeric complexes are obtained from the reaction of $(MeCN)_2PdCl_2$ with (Ib). Conventional metathetical reactions of (II) and (III) yield the corresponding complexes (IV)† and (V)‡ respectively.

Formation of complexes (II) and (III) can be rationalised by formation of an intermediate 1,2-η-bonded methylenecyclopropane complex of Pd^{II} [see Scheme]. Intramolecular nucleophilic attack by chloride on the internal olefinic carbon, followed by electrophilic attack by palladium on the 1,2-bond of the cyclopropane ring, leads to a stereospecific ring-opening and formation of (II). In methanol, however, attack by the external solvent nucleophile on the exocyclic olefinic carbon must be invoked. Hydride transfer, followed by electrophilic ring-opening by palladium, yields

† Satisfactory n.m.r. data were obtained.

‡ Complex (V) exists as two isomers (ratio 1 : 1) in solution, differing in the conformation of the CO_2Me groups with respect to the co-ordinated olefin. The isomer ratio in (III) is 2 : 1.

(III). The difference in stereochemical direction of attack by internal and external nucleophiles is highly reminiscent of the reaction of allenes with Pd^{II} systems.[8] Cleavage of the 1,2-bond in (Ia) contrasts with the reported[4] cleavage of the 2,3-bond in 2,2-diphenylmethylenecyclopropane. Complexes (II)—(V) represent the first examples of 1,3-enyl transition metal complexes, and the possibility of π-homoallylic bonding in these ligands is being investigated crystallographically.

Complexes (II)—(V) react with donor ligands, such as pyridine, to yield the Pd^{II}–alkyl complexes (VI)—(IX) [Scheme] as stable crystals.† The stability of these complexes is surprising since there is a β-hydrogen available on the alkyl group for elimination. The value of the vicinal coupling constant ($J_{1,2}$ 12 Hz) in complex (VI) is invariant from $-60°$ to $+60°$, implying an appreciable barrier to free rotation about the carbon–carbon σ-bond imposed by the bulkiness of the substituents. Such conformational restriction presumably prevents the palladium and β-hydrogen atoms from attaining the required relative stereochemistry for elimination to occur, and represents a novel concept in the stabilisation of transition-metal alkyl bonds. In principle, this concept explains the stabilisation of metal–alkyl bonds at normal temperatures, but does not preclude β-hydrogen elimination at temperatures at which the rotational energy barrier can be overcome. The detailed conformation of the alkyl chain in (VI) is being determined crystallographically.§

Finally, the complexes (X) and (XI), isolated from reactions of (II) and (III) with 1,5-cyclo-octadiene, represent stable alkyl π-olefin complexes of palladium(II). No insertion of the olefin into the Pd-C σ-bond occurs on standing in solution for several days. Further studies of the chemistry of these complexes are in progress.

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§ Although contributions to the stability of complexes (VI)—(IX) may be derived from the presence of electronegative CO_2Me groups on the alkyl chain, the observation that these compounds thermally rearrange at higher temperatures (*ca.* 80°) indicates that is not an overriding factor. Studies of these thermal rearrangements are in progress.

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