Journal of Organometallic Chemistry, 184 (1980) C67—C69

Preliminary communication

THE CHLOROPALLADATION OF 2,2-DIPHENYLMETHYLENECYCLOPROPANES

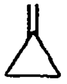
BRUCE K. DALLAS and RUSSELL P. HUGHES*
Department of Chemistry, Dartmouth College, Hanover, N.H. 03755 (U.S.A.)

(Received October 2nd, 1979)

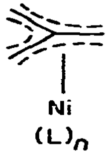
Summary

Chloropalladation of 2,2-diphenyl-3,3-dideuteromethylenecyclopropane is shown to proceed via an unsymmetrically complexed trimethylenemethane species.

The recent upsurge of interest in transition metal promoted reactions of strained organic rings has resulted in attention being focussed on the reactions of methylenecyclopropane I and its substituted analogs. Under the influence of transition metal compounds methylenecyclopropanes have been shown to undergo catalytic dimerization and codimerization reactions in which the cyclopropane ring remains intact, or in which one of the carbon—carbon bonds of the cyclopropane ring is cleaved [1]. Recent work on the nickel(0)-catalyzed reactions of I has demonstrated unambigously that cleavage of the 2,3-bond of the cyclopropane ring in I results in the generation of a symmetrically bound η^4-trimethylenemethanenickel species (II) [2]. Similar intermediates have been proposed in the palladium(0) promoted reactions of I [3].



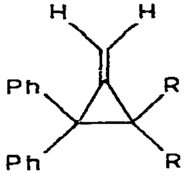
(I)

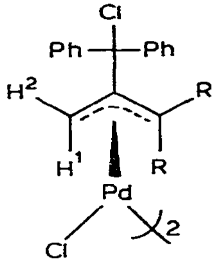


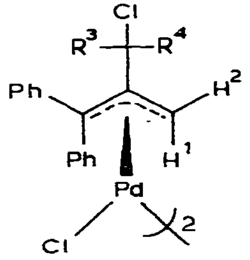
(II)

We have described stoichiometric chloropalladations of methylenecyclopropanes in which cleavage of the cyclopropane ring can occur in a 1,2- or a 2,3-fashion, depending upon the nature of substituents on the ring [4,5]. Chloropalladation of 2,2- or 2,3-dialkylmethylenecyclopropanes occurred exclusively by

2,3-cleavage of the ring; a zwitterionic, unsymmetrically coordinated trimethylenemethane intermediate was proposed to account for these observations [5]. However, previously reported results on the chloropalladation of 2,2-diphenylmethylenecyclopropane (IIIa) [6] could not be reconciled [5] with such an intermediate. We have reinvestigated this latter reaction and find the reported observations to be incomplete.

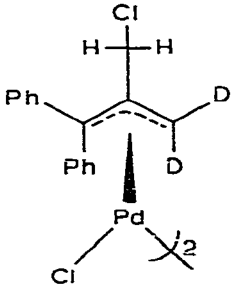

(IIIa, R = H;
IIIb, R = D)

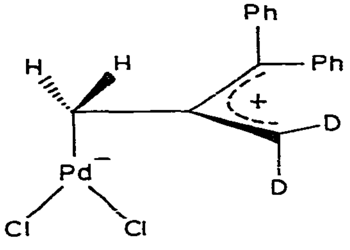

(IVa, R = H;
IVb, R = D)

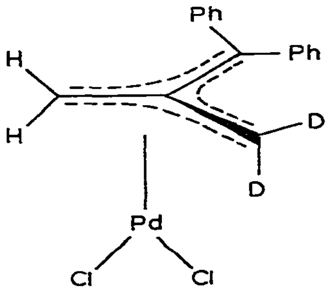

(Va, R = H;
Vb, R = D)

Reaction of equimolar amounts of IIIa* with $PdCl_2(PhCN)_2$ occurred almost instantly (CH_2Cl_2 or $CDCl_3$ solution; 20°C) to afford a 1/1 mixture of IVa and Va**. Subsequent rapid isomerization of IVa to Va occurred via a process shown to be kinetically first-order in palladium (k_{obs} (20°C) = 4.6×10^{-4} sec^{-1}). Under identical conditions the deuterated methylenecyclopropane (IIIb)*** reacted with $PdCl_2(PhCN)_2$ to give initially a 1/1 mixture of IVb and Vb. After subsequent isomerization of IVb was complete the final product mixture contained only Vb and VI in a 3/1 ratio. No VI was observed in the initial product mixture.

In light of our previous observations on the chloropalladation of alkylmethylenecyclopropanes [5], these results can only be reconciled with the generation


(VI)


(VII)


(VIII)

---

*Prepared from 1,1-diphenylethylene by the method of Arora and Binger [7].

**^1H NMR data (270 MHz; $CDCl_3$; 20°C) for IVa and Va, numbering given in text: IVa δ 3.50 (s, H_1); 4.14 (s, H_2); 4.30, 3.98 (AB quartet, J ca. 12 Hz, H_3 and H_4; 7.30 (m, Ph): Va δ 3.02 (s, H_1); 3.84 (s, H_2); 7.30 (m, Ph).

***Prepared from IIIa by treatment with $CD_3SOCD_2^-/CD_3SOCD_3$ [8]. The resultant IIIb had 75% D at the cyclopropane carbon.

of an unsymmetrically complexed trimethylenemethane (VII), followed by intramolecular chloride migration to either terminus of the allylic cation. A symmetrically complexed η^4-trimethylenemethane species VIII is ruled out by the absence of VI in the initially formed product mixture. Isomerization of IVb to a 1/1 mixture of Vb and VI without concomitant isomerization of initially formed Vb to VI explains the observed final 3/1 ratio of Vb/VI.

An unsymmetrically complexed trimethylenemethane species analogous to VII, formed by initial attack of a transition metal at the olefinic function of methylenecyclopropanes, may well be a precursor to the η^4-trimethylenemethane-metal species which are apparently active in catalytic systems [2,3]. Previous workers have implied that such species are formed by initial attack of the metal at the cyclopropane ring [2,3].

Acknowledgements

We acknowledge support of this work by the National Science Foundation (Grant No. CHE77-17877). Support of the Southern New England High Field NMR Facility, made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR 798) is also appreciated.

References

1 (a) R. Noyori, T. Odagi and H. Takaya, J. Amer. Chem. Soc., 92 (1970) 5780; (b) R. Noyori, Y. Kumagai, I. Umeda, and H. Takaya, ibid., 94 (1972) 4018; (c) H. Takaya, N. Hayashi, T. Ishigami and R. Noyori, Chem. Lett., (1973) 813; (d) R. Noyori, T. Ishigami, N. Hayashi and H. Takaya, J. Amer. Chem. Soc., 95 (1973) 1674; (e) P. Binger and J. McMeeking, Angew. Chem., Int. Ed. Engl., 12 (1973) 995; (f) P. Binger, Synthesis, (1973) 427.
2 R. Noyori, M. Yamakawa and H. Takaya, Tetrahedron Lett., (1978) 4823.
3 P. Binger and U. Schüchardt, Angew. Chem., Int. Ed. Engl., 16 (1977) 249.
4 (a) M. Green and R.P. Hughes, J. Chem. Soc. Dalton, (1976) 1880; (b) M. Green and R.P. Hughes, ibid., (1976) 1890.
5 R.P. Hughes, D.E. Hunton and K. Schumann, J. Organometal. Chem., 169 (1979) C37.
6 R. Noyori and H. Takaya, Chem. Commun., (1969) 525.
7 S. Arora and P. Binger, Synthesis, (1974) 801.
8 W.D. Slafer, A.D. English, D.O. Harris, D.F. Shellhamer, M.J. Meshishnek and D.H. Aue, J. Amer. Chem. Soc., 97 (1975) 6638.