Journal of Organometallic Chemistry, 96 (1975) C23—C26

Preliminary communication

THE ROLE OF NICKELOLE INTERMEDIATES IN THE OLIGOMERIZATION OF ALKYNES

JOHN J. EISCH* and JAMES E. GALLE

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901 (U.S.A.)

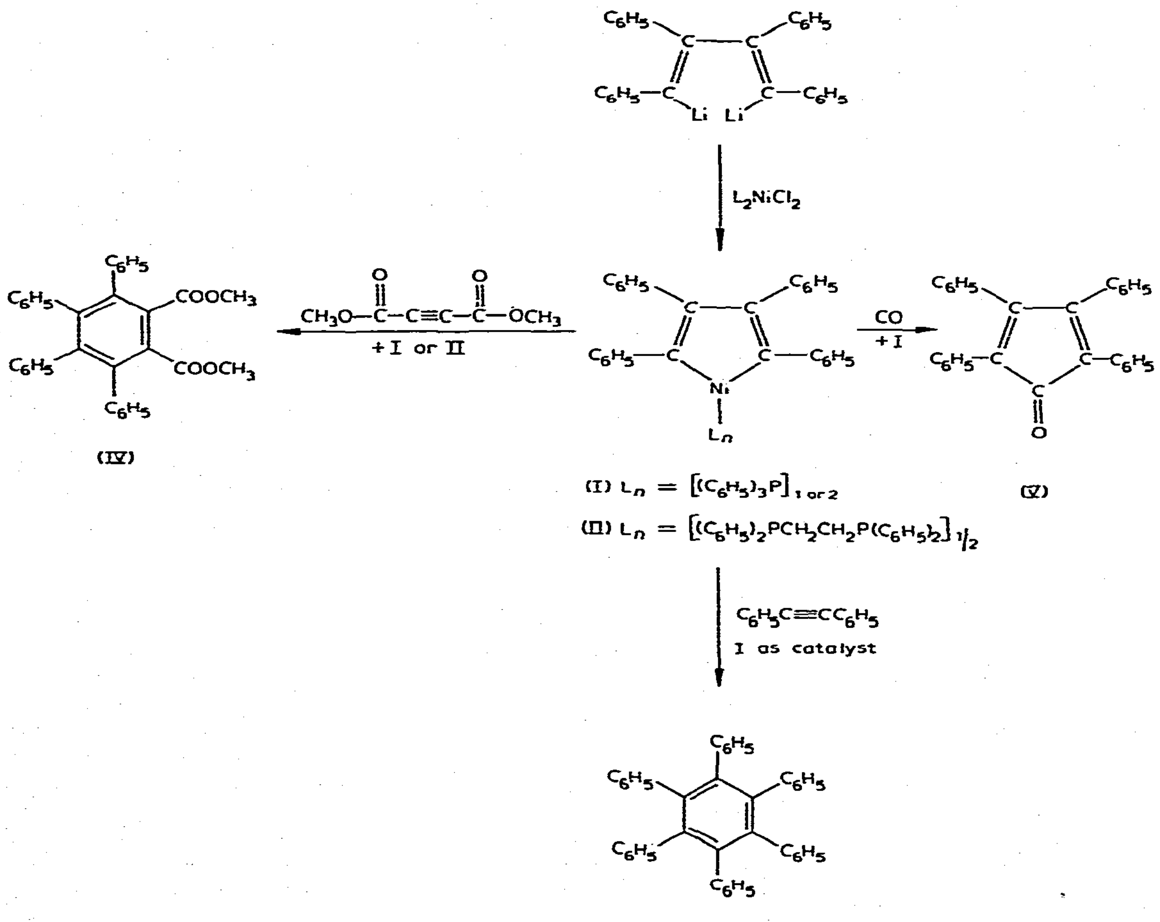
(Received May 9th, 1975)

Summary

Bis(triphenylphosphine)nickel(II) chloride reacts with *E*,*E*-1,4-dilithio-1,2,3,4-tetraphenylbutadiene to yield a solution of a 2,3,4,5-tetraphenylnickelole complex. This compound reacts promptly with CO to yield tetracyclone, with dimethyl acetylenedicarboxylate to form dimethyl tetraphenylphthalate and catalytically with diphenylacetylene to form hexaphenylbenzene. A similar treatment of (1,2-bis(diphenylphosphino)ethane)nickel(II) chloride with the lithium reagent led to the isolation of (1,2-bis(diphenylphosphino)ethane)bis(2,3,4,5-tetraphenylnickelole), which likewise reacts with dimethyl acetylenedicarboxylate to yield dimethyl tetraphenylphthalate. These results support the interpretation that nickeloles are reactive intermediates in the cyclotrimerization of alkynes by nickel(0) catalysts.

Despite much interest in the mechanisms of alkyne oligomerizations by transition-metal catalysts [1], little attention has been given to the modes by which nickel(0) catalysts trimerize alkynes. The intermediacy of metallole or metallole-like systems has been demonstrated or inferred for the cyclotrimerizations of alkynes by Ir [2a], Rh [2a, b], Pd [3], Cr [4a], Co [4a, b], Ni (4a, 5] and Ti [4a]. On the other hand, an intermediate of cyclobutadiene-like symmetry seems to be involved in trimerizations promoted by aluminum(III) [4a, 6] or palladium(II) salts [4a, 7]. With palladium halides, apparently palladole, π-cyclobutadienepalladium complexes and linear alkyne trimer-chloropalladation adducts can all occur as metastable precursors to the alkyne cyclotrimers [4, 7].

A recent study of the alkylation of alkynes by bis(π-allyl)nickel has uncovered evidence of alkyne-dimerization and -cyclotrimerization by nickel(0) and has led to the postulation of a nickelole intermediate in such oligomerizations [5a]. Therefore, we set out to prepare the unknown nickelole ring system, in order to investigate its chemical properties and its catalytic activity toward alkynes. Thus, the interaction of 3.0 mmol of *E*,*E*-1,4-dilithio-1,2,3,4-tetraphenylbutadiene (prepared and isolated beforehand as the crystalline yellow dietherate), which was dissolved in 50 ml of diethyl ether, with 2.95 mmol of bis(triphenylphosphine)nickel(II) chloride at 25 °C gave complete reaction after 15 min to yield a reddish brown, air-sensitive solution of the presumably complexed 2,3,4,5-tetraphenylnickelole (I). Analogously, a freshly prepared solution of 3.6 mmol of the dilithium reagent in 75 ml of methylene chloride (stable for short periods) was added to a suspension of 3.3 mmol of (1,2-bis(diphenylphosphino)ethane)nickel(II) chloride at 25°. The mixture became homogeneous briefly and then the brick-red solid precipitated almost quantitatively. After washing successively with methanol, toluene and ether, the highly insoluble, halogen-free compound gave satisfactory carbon and hydrogen analyses and values for nickel and phosphorus in better accord with the composition of (1,2-bis(diphenylphosphino)ethane)bis(2,3,4,5-tetraphenylnickelole) (II) (Found: Ni, 10.3; P, 6.3. Calcd.: Ni, 9.6; P, 5.0%.), than with a 1/1 nickelole-1,2-bis(diphenylphosphino)ethane complex (Calcd.: Ni, 7.2; P, 7.6.). The marked insolubility and extreme air-sensitivity of II hindered further purification. Although the low volatility of II vitiated mass spectral data on its molecular weight (only the parent ions of $(C_6H_5C{\equiv}CC_6H_5)_n$



SCHEME 1

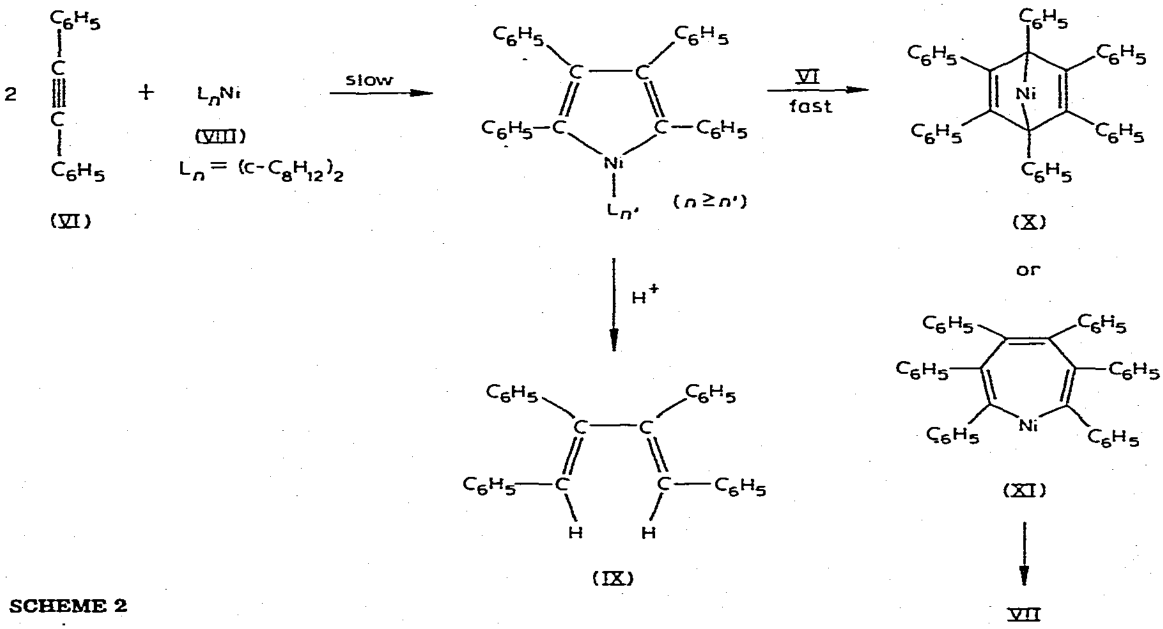
were readily detectable, where n = 1-4), II had an intense IR band at 1585 cm^{-1}. This absorption seems characteristic of the M—C=C grouping [8][*].

Both I and II reacted readily with excess dimethyl acetylene dicarboxylate (III) to yield ca. 60% of dimethyl tetraphenylphthalate (IV). The benzene-soluble nickelole I reacted with three equiv. of CO at 25 °C to give tetracyclone (V) in 68% yield; a suspension of the insoluble II was unreactive to CO under these conditions. Furthermore, heating diphenylacetylene (VI) (40 mmol) with I (1.3 mmol) caused the reddish-brown color of I to give way rapidly to a light yellow color and more slowly to cause precipitation of hexaphenylbenzene (VII). An 82% yield of VII was formed after 15 h (Scheme 1).

The behavior of a nickel(0) catalyst, bis(1,5-cyclooctadiene)nickel (VIII) [9], toward diphenylacetylene closely paralleled the behavior of I. Thus, diphenylacetylene was readily trimerized to VII when heated with 2% of VIII. When this acetylene was treated with 0.5 equiv. of VIII for short periods and the reaction mixture worked up with acid, both the trimer VII and *E,E*-1,2,3,4-tetraphenylbutadiene (IX) were formed. These observations on the reactivitiy of preformed nickeloles toward alkynes, taken together with the detection of reductive dimers of alkynes in this and in the foregoing study [5], can be adduced as strong evidence for the following mechanistic pathway (Scheme 2).

Whether X or XI is the principal unstable intermediate is uncertain. But structure XI should seem able to insert further VI, leading to an alkyne tetramer. The absence of such tetramer thus seems to speak in favor of X.

Finally, the mixed cyclooligomers formed between two moles of alkyne and alkenes or 1,3-alkadienes [10] can also be explained as arising from nickelole intermediates.



SCHEME 2

---

[*] Many metalloles and related systems are reported to have moderate to intense infrared bands in the 1530-1600 cm^{-1} region, which appear to be associated with the vinylic-metal grouping [2a, 8].

Acknowledgements

The authors wish to express appreciation to The National Science Foundation for the support of this research under Grant GP-34204.

References

1 C.W. Bird, Transition Metal Intermediates in Organic Synthesis, Academic Press, New York, N.Y., 1967, Chap. 1.
2 (a) J.P. Collman, J.W. Kang, W.F. Little and M.F. Sullivan, Inorg. Chem., 7 (1968) 1298; (b) S.A. Gardner and M.D. Rausch, J. Organometal. Chem., 78 (1974) 415.
3 K. Moseley and P.M. Maitlis, Chem. Commun., (1971) 1604.
4 (a) G.M. Whitesides and W.J. Ehmann, J. Amer. Chem. Soc., 91 (1969) 3800; (b) H. Yamazaki and N. Hagihari, J. Organometal. Chem., 21 (1970) 431.
5 (a) J.J. Eisch and G.A. Damasevitz, J. Organometal. Chem. 96 (1975) C19; (b) J. Browning, C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc., A (1971) 448; (c) J. Browning, M. Green, B.R. Penfold, J.L. Spencer and F.G.A. Stone, Chem. Commun., (1973) 31.
6 C. Krüger, P.J. Roberts, Y.-H. Tsay and J.B. Köster, J. Organometal. Chem., 78 (1974) 69.
7 H. Dietl, H. Reinheimer, J. Moffat and P.M. Maitlis, J. Amer. Chem. Soc., 92 (1970) 2276.
8 (a) W. Keim, J. Organometal. Chem., 16 (1969) 191, but cf. J.S. Ricci and J.A. Ibers, J. Organometal. Chem., 27 (1971) 261; (b) T.G. Mague and G. Wilkinson, Inorg. Chem., 7 (1968) 542; (c) S.A. Gardner, P.S. Andrews and M.D. Rausch, Inorg. Chem., 12 (1973) 2396.
9 B. Bogdanović, M. Kröner and G. Wilke, Justus Liebigs Ann. Chem., 699 (1966) 1.
10 P. Heimbach, Angew. Chem., 85 (1974) 105.