

## Novel Cycloaddition Reactions of Isocyanides with Diphenylacetylene Using Transition-metal Complexes

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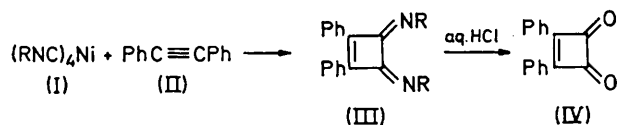
**Summary** Reaction of tetrakis(aryl isocyanide)nickel complexes (Ia—c) with diphenylacetylene gave the diiminocyclobutenes (IIIa—c); on pyrolysis, the acetylene complex (Va) gave (IIIa) as sole product, while with (Vd) the major product was iminocyclopentadiene (VIId).

to give tri-iminocyclopentene and pyridine derivatives, whereas aryl and alkyl substituted acetylenes were unreactive, probably owing to the lower electron affinity of their triple bonds.<sup>1</sup> As the isocyano-group is isoelectronic with carbon monoxide and reactions of various metal carbonyls with carbon monoxide and reactions of various metal carbonyls with acetylenes are well known,<sup>2</sup> it was expected that the reactions of isocyanides with diphenyl-

WE previously reported the cycloadditions of isocyanide to acetylenes substituted with electron-withdrawing groups

acetylene would give cyclized products *via* co-ordination to a transition metal.

An equimolar mixture of (Ia)<sup>3</sup> and diphenylacetylene (II) was refluxed in toluene for 1 h under nitrogen. Addition of n-hexane and chromatography of the filtrate yielded the yellow di-iminocyclobutene (IIIa), m.p. 205–206°, [30% based on (II)]. Its structure was established by elemental analysis, molecular weight determination, and its i.r., u.v.,

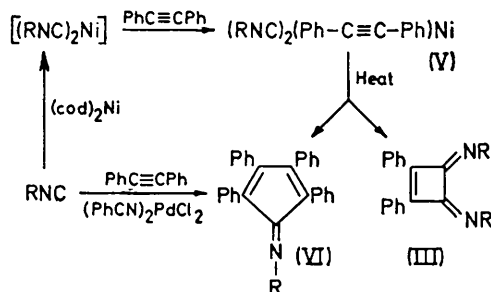


a; R = 2,6-Me<sub>2</sub>,4-BrC<sub>6</sub>H<sub>2</sub>    b; R = Ph    c; R = *p*-MeO·C<sub>6</sub>H<sub>4</sub>

and n.m.r. spectra. Hydrolysis of (IIIa) with aqueous HCl gave diphenylcyclobutenedione (IV), identical with an authentic sample.<sup>4</sup> The tetrakis(aryl isocyanide)nickel complexes (Ib and c) reacted with acetylene (II) to give the di-imino-cyclobutenes (IIIb), m.p. 158–160° (90%) and (IIIc), m.p. 169–171° (22%). Under similar conditions, tetrakis-(*t*-butyl isocyanide)nickel<sup>5</sup> and tetrakis-(2,6-dimethylphenyl isocyanide)nickel were unreactive to (II).

A mixed ligand complex of isocyanide and acetylene formed initially is possibly an important intermediate in the formation of (III). Bis(cyclo-octa-1,5-diene)nickel [(cod)<sub>2</sub>-Ni] reacted readily with 2 mol. equiv. of the isocyanide in toluene at room temperature and subsequent addition of 1 mol. equiv. of (II) gave yellow microcrystals of (Va) [ $\nu(\text{N}\equiv\text{C})$  2160 and 2100 cm<sup>-1</sup>;  $\nu(\text{C}\equiv\text{C})$  1830 cm<sup>-1</sup>] whose i.r. spectrum is similar to that of the known complex (Ve).<sup>6</sup> Heating of complex (Va) at 80–100° in toluene gave

di-iminocyclobutene (IIIa) (30%). However, pyrolysis of complex (Vd), prepared similarly, in toluene gave the cyclopentadiene (VIId) as dark violet crystals, m.p. 190–



a; R = 2,6-Me<sub>2</sub>,4-BrC<sub>6</sub>H<sub>2</sub>    c; R = *p*-MeO·C<sub>6</sub>H<sub>4</sub>  
d; R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>    e; R = Bu<sup>1</sup>

191° (65%), together with a small amount of (IIIId), m.p. 175–177°. The structure of (VIId) was supported by elemental analyses and hydrolysis with aqueous HCl to tetracyclone, as well as its i.r., u.v., and n.m.r. spectral data.

Reaction of the isocyanides R-NC (R as in a, c, and d) with (II) in the presence of bis(benzonitrile)palladium chloride (molar ratio 1:2:1) gave the iminocyclopentadienes (VIa), m.p. 186–187° (VIc), m.p. 206–207°, and (VIId) in 21, 10, and 14% yield, respectively, in addition to the known palladium complex of tetraphenylcyclobutadiene, Pd<sub>3</sub>Cl<sub>3</sub>(Ph<sub>4</sub>C<sub>4</sub>)<sub>2</sub>,<sup>7</sup> (30–40% based on Pd).

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