

## Diazoalkane-Nickel(0) Complexes

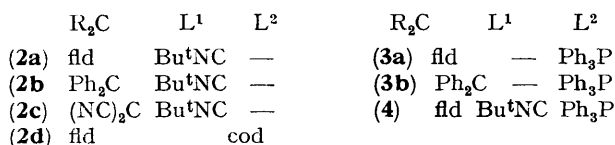
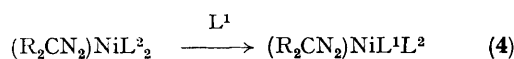
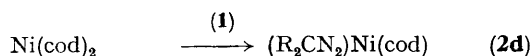
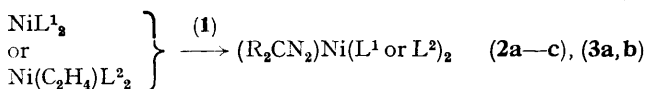
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**Summary** The preparation, characterisation, and thermal decomposition of a series of the title complexes are reported.

DIAZOALKANES (1) react with various metal complexes generally with the extrusion of dinitrogen;<sup>1</sup> some transition-metal complexes containing the azine group (>C=N-N=C<) have been isolated.<sup>2</sup> However, discrete metal complexes containing (1) are as yet unknown. These complexes† may have an important bearing on metal carbenoid reactions.

We have prepared a series of diazoalkane complexes of nickel(0)† by routes shown below. The isocyanide complexes (2a–c) are very sensitive to air even in the crystalline state, but not very unstable thermally except for the cyclo-octa-1,5-diene complex (2d) whose extreme instability in solution prevented detailed characterization. The corresponding palladium complexes are even more unstable. (Diazo fluorene)PdBu<sup>t</sup>(NC)<sub>2</sub> readily decomposes above –20° in the solid state.

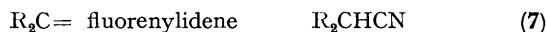
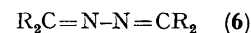
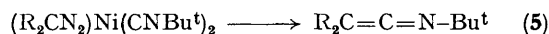


cod: cyclo-octa-1,5-diene; fld = fluorenylidene.

I.r. and <sup>1</sup>H n.m.r. spectra show that these Ni<sup>0</sup> complexes are isostructural, and the <sup>1</sup>H n.m.r. spectra [(CD<sub>3</sub>)<sub>2</sub>CO] of

(2a and b) confirm their stoichiometry and diamagnetic nature. The strong i.r. band in the 1480–1520 cm<sup>-1</sup> region [ν (co-ordinated >C=N=N)] excludes a linear end-on co-ordination involving a lone pair on the terminal nitrogen, which would give rise to a peak at 2000–2200 cm<sup>-1</sup>. Side-on co-ordination of the C=N=N system is likely. This i.r. frequency (1480–1520 cm<sup>-1</sup>) decreases as the electron-releasing ability of the auxiliary ligand increases. The NC stretching vibrations of the isocyanide ligands<sup>3</sup> in (2a) and (2b) are higher than that in the zero-valent parent compound, indicating electron withdrawal from metal to the diazoalkane ligand. The occurrence of the substitution reaction suggests that (1) co-ordinates to the metal without skeletal change. Thus, the original diazoalkane in (2a) is readily regenerated by reaction with oxygen or triphenylphosphine. The exact molecular structure is being investigated by X-ray analysis.

Thermal decomposition of (2a) in toluene at 100° gave a mixture of (5) (44%), (6) (10%), and (7) (23%). Under comparable conditions, diazo fluorene and t-butyl isocyanide, in the absence of a metal complex, gave a small amount of the ketazine (6) only.



Cationic d<sup>10</sup> metal complexes, e.g. (1,5-C<sub>8</sub>H<sub>12</sub>)AgNO<sub>3</sub> or (1,5-C<sub>8</sub>H<sub>12</sub>)CuCl, do not form an analogous complex stable enough to be isolated. On dropwise addition of diazo fluorene into an equimolar quantity of these salts in benzene at 20°, bifluorenylidene was formed in good yield (89–94%). Cyclopropane formation *via* a carbenoid reaction with the co-ordinated or free added cyclo-octa-1,5-diene was not observed.

† All new nickel complexes gave satisfactory analytical results.

A somewhat different reaction occurred when  $\text{Ni}(\text{Bu}^t\text{NC})_4$  was treated with  $\text{N}_2\text{C}(\text{CN})_2$  at  $-78^\circ$  to  $-40^\circ$  in ether when a purple precipitate was formed which changed to yellow on further warming. The yellow crystalline product,  $[\text{Ni}(\text{Bu}^t\text{NC})_3\text{C}(\text{CN})_2]_2$ , m.p.  $173-175^\circ$ , was relatively stable in air. I.r. and n.m.r. spectra showed the presence of terminal and bridging isocyanide ligands in a 2:1 ratio.

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<sup>2</sup> J. Clemens, R. E. Davis, M. Green, J. D. Oliver, and F. G. A. Stone, *Chem. Comm.*, 1971, 1095.

<sup>3</sup> S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1971, **93**, 6462; *Chem. Comm.*, 1971, 67.