Diazoalkane–Nickel(0) Complexes

By SEI OTSUKA,* AKIRA NAKAMURA, TERUHISA KOYAMA, and YOSHITAKA TATSUNO
(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)

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;[1] some transition-metal complexes containing the azine group ($>C=N-N=C<$) have been isolated.[2] 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. (Diazofluorene)$PdBu^t(NC)_2$ readily decomposes above −20° in the solid state.

$$\left.\begin{array}{l}NiL^1_2\\ \text{or}\\ Ni(C_2H_4)L^2_2\end{array}\right\}\xrightarrow{(\mathbf{1})}(R_2CN_2)Ni(L^1\text{ or }L^2)_2\qquad(\mathbf{2a}\text{—}\mathbf{c}),\ (\mathbf{3a,b})$$

$$Ni(cod)_2\xrightarrow{(\mathbf{1})}(R_2CN_2)Ni(cod)\qquad(\mathbf{2d})$$

$$(R_2CN_2)NiL^2_2\xrightarrow{L^1}(R_2CN_2)NiL^1L^2\qquad(\mathbf{4})$$

	R_2C	L^1	L^2		R_2C	L^1	L^2
(**2a**)	fld	Bu^tNC	—	(**3a**)	fld	—	Ph_3P
(**2b**	Ph_2C	Bu^tNC	—	(**3b**)	Ph_2C	—	Ph_3P
(**2c**)	$(NC)_2C$	Bu^tNC	—	(**4**)	fld	Bu^tNC	Ph_3P
(**2d**)	fld	cod					

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

I.r. and ^1H n.m.r. spectra show that these Ni^0 complexes are isostructural, and the ^1H n.m.r. spectra [$(CD_3)_2CO$] of (**2a** and **b**) confirm their stoicheiometry and diamagnetic nature. The strong i.r. band in the 1480—1520 cm^{-1} 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^{-1}. Side-on co-ordination of the $C=N=N$ system is likely. This i.r. frequency (1480—1520 cm^{-1}) decreases as the electron-releasing ability of the auxiliary ligand increases. The NC stretching vibrations of the isocyanide ligands[3] 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, diazofluorene and t-butyl isocyanide, in the absence of a metal complex, gave a small amount of the ketazine (**6**) only.

$$\begin{array}{lll}(R_2CN_2)Ni(CNBu^t)_2\longrightarrow & R_2C=C=N\text{–}Bu^t & (\mathbf{5})\\ & R_2C=N\text{–}N=CR_2 & (\mathbf{6})\\ R_2C=\text{ fluorenylidene} & R_2CHCN & (\mathbf{7})\end{array}$$

Cationic d^{10} metal complexes, *e.g.* $(1,5\text{-}C_8H_{12})AgNO_3$ or $(1,5\text{-}C_8H_{12})CuCl$, do not form an analogous complex stable enough to be isolated. On dropwise addition of diazofluorene 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.

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† All new nickel complexes gave satisfactory analytical results.

A somewhat different reaction occurred when $Ni(Bu^tNC)_4$ was treated with $N_2C(CN)_2$ at −78° to −40° in ether when a purple precipitate was formed which changed to yellow on further warming. The yellow crystalline product, $[Ni(Bu^tNC)_3C(CN)_2]_2$, m.p. 173—175°, 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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