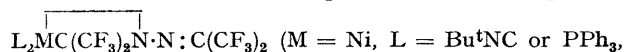


Reactions of Bis(trifluoromethyl)diazomethane with Zerovalent Nickel, Palladium, and Platinum Complexes

By J. CLEMENS, R. E. DAVIS,*† M. GREEN, J. D. OLIVER,† and F. G. A. STONE*

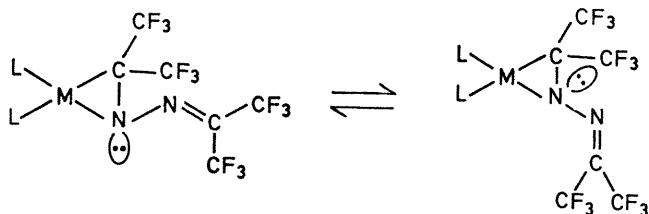
(*Department of Inorganic Chemistry, The University, Bristol BS8 ITS, and the †Department of Chemistry, University of Texas at Austin, Austin 78712*)

Summary Bis(trifluoromethyl)diazomethane reacts with zerovalent Ni, Pd, or Pt complexes to afford compounds



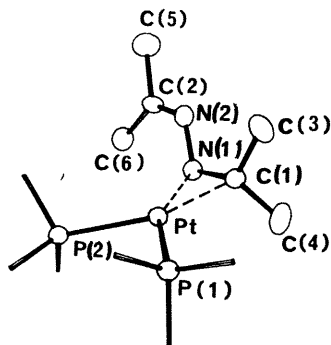
$\text{L}_2 = 1,5\text{-C}_8\text{H}_{12}$; $\text{M} = \text{Pd}$, $\text{L} = \text{Bu}^t\text{NC}$ or $\text{C}_6\text{H}_{11}\text{NC}$; $\text{M} = \text{Pt}$, $\text{L} = \text{PPh}_3$); the structure of the platinum complex was established by a single crystal X-ray diffraction study.

BIS(TRIFLUOROMETHYL) DIAZOMETHANE,¹ a possible source of the electrophilic carbene $(CF_3)_2C$, reacts at room temperature with tetrakis(*t*-butyl isocyanide)nickel, ethylenebis(triphenylphosphine)nickel, bis(cyclo-octa-1,5-diene)nickel, bis(*t*-butyl isocyanide)palladium, bis(cyclohexyl isocyanide)palladium, tetrakis(triphenylphosphine)platinum, and stilbenebis(triphenylphosphine)platinum to form respectively complexes (I)—(VI),² having the general formula $L_2M-[C_2N_2(CF_3)_4]$. Except for (II) and (III), the complexes are air and thermally stable, and their i.r., ¹H, and ¹⁹F n.m.r. spectra indicated that they are all isostructural. *E.g.*, yellow crystalline (VI) [m.p. 196—197° (decomp.)] showed ν_{max} at 1560s cm^{-1} , indicative of the $N:C(CF_3)_2$ group; the ¹⁹F n.m.r. spectrum showed three resonances at 59.5 (d with ¹⁹⁵Pt satellites, 6F, J_{PF} 10.0 Hz, J_{PtF} 79.0 Hz), 63.5 (m, 3F, J_{PF} 6.0 Hz, J_{FF} 2.5 Hz) and 65.8 (apparent quintet, 3F, J_{PF} 6.0 Hz, J_{FF} 6.0 Hz) p.p.m. (relative to CCl_3F). Double irradiation of the high-field band collapsed the multiplet at 63.5 p.p.m. to a doublet (J_{PF} 6.0 Hz), whereas irradiation of the band at 65.8 p.p.m. caused the collapse of the high-field band to a doublet (J_{FF} 2.5 Hz).



- (I; M = Ni, L = Bu⁴NC)
 (II; M = Ni, L = PPh₃)
 (III; M = Ni, L₂ = 1,5-C₈H₁₂)
 (IV; M = Pd, L = Bu⁴NC)
 (V; M = Pd, L = C₆H₁₁NC)
 (VI; M = Pt, L = PPh₃)

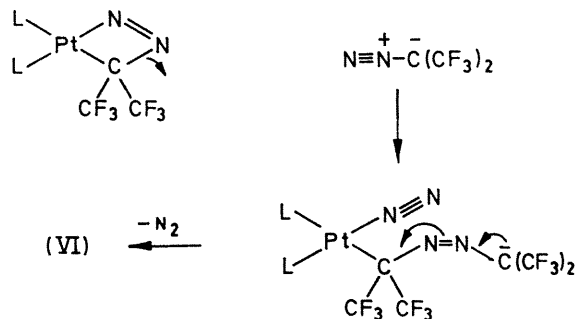
These observations suggested the illustrated structure where the azine $(CF_3)_2C:N:N:C(CF_3)_2$ ³ is co-ordinated *via* one of the carbon–nitrogen double bonds to the metal. Support for this was provided by the observation that treatment of (VI) with iodine in benzonitrile afforded $PtI_2(PPh_3)_2$ and the azine $(CF_3)_2C:N:N:C(CF_3)_2$. Reaction of the free azine with stilbenebis(triphenylphosphine)platinum regenerated (VI), there being no evidence for a 1,4-addition. However, a serious difficulty with the illustrated structure is



FIGURE

that the ¹⁹F n.m.r. spectrum of (VI) requires that on the n.m.r. time scale (even at -80°) the CF_3 groups attached to the carbon adjacent to the platinum are in identical environments. In order to clarify this important question and to confirm with certainty the identity of this new type of complex a single crystal X-ray diffraction study was undertaken.

Crystals of (VI) from methylene chloride are monoclinic, $C2/c$ with $a = 31.155$, $b = 13.091$, $c = 21.828$ Å, $\beta = 109.24^\circ$, $Z = 8$. Using the 5046 observed reflections of 5793 measured with $Cu-K\alpha$ radiation, the structure was solved by the heavy-atom method, the co-ordinates of the Pt and two P atoms having been obtained from a Patterson map. The structure has been refined, including CH_2Cl_2 at occupancy *ca.* 0.4 on a crystallographic 2-fold axis, to a conventional R value of 0.056 and a weighted R value of 0.059. The molecular geometry is shown in the Figure, from which the 12 F



atoms of the trifluoromethyl groups and the 30 phenyl C atoms not bonded to P atoms have been omitted. The PtC(1) and PtN(1) distances are 2.02 and 2.11 Å, respectively. The C(1)N(1) distance (1.44 Å) is similar to the CN distance in aziridine (1.488 Å).⁴ The interplanar angles shown in the Table may be compared with a uniform value of

TABLE		R.m.s. distance from plane (Å)
Plane	Atoms	
1	Pt, C(1), N(1)	0
2	N(1), N(2), C(1), C(2), C(3), C(5), C(6)	0.02
3	N(1), C(1), C(4)	0
Planes	Interplanar angle (°)	
1,2	119	
1,3	114	
2,3	127	

120° for idealized sp^3 hybridization of C(1) and N(1). The 36 phenyl C–C distances average 1.41 ± 0.03 Å, the 12 C–F distances average 1.32 ± 0.03 Å, and the six P–C distances average 1.82 ± 0.02 Å.†

In order to reconcile the observed structure of (VI) in the solid state and the equivalence of two of the CF_3 groups in solution, it is necessary to postulate that in solution rapid inversion occurs at the nitrogen bonded to the platinum. conjugation with the $N=C(CF_3)_2$ group, or more likely, due This contrasts with the quite high barriers to inversion observed⁵ with aziridines. This effect may be due to

† The structure and further details of the molecular geometry will be published elsewhere (J. D. O. and R. E. D.).

to interaction of the nitrogen lone pair with an empty platinum $6p$ orbital. We have yet to establish the mechanism for the formation of the azine complexes; however, an interesting possibility is that the diazo-compound reacts as a 1,3-dipolarophile to form a four-membered ring compound. Cleavage of the carbon-nitrogen bond with concomitant attack on a further $(\text{CF}_3)_2\text{CN}_2$ molecule is then facilitated by stabilization of the co-ordinated nitrogen.

Formation of complexes (I)–(VI) contrasts with the nature of the products obtained from reactions between bis-

(trifluoromethyl)diazomethane and other transition-metal complexes^{6,7} where non-nitrogen containing products are obtained and the carbene $(\text{CF}_3)_2\text{C}$ is implicated.

We thank the S.R.C. for a studentship (J. C.) and N.A.S.A. for a predoctoral traineeship (J. D. O.). Thanks are also due to the Robert A. Welch Foundation for support of the X-ray crystallographic study.

(Received, July 2nd, 1971; Com. 1116.)

¹ D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **1966**, **88**, 3617.

² Complex (VI) has been independently obtained by Lappert and his co-workers; see D. J. Cardin, B. Cetinkaya, M. F. Lappert, L. J. ManojLović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

³ W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **1965**, **30**, 1398.

⁴ T. C. Turner, V. C. Fiora, and W. C. Kendrick, *J. Chem. Phys.*, **1955**, **23**, 1966.

⁵ A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, **1970**, **9**, 400.

⁶ J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, **1969**, 1872.

⁷ J. A. Smith, J. Clemens, M. Green, and F. G. A. Stone, *J. Organometallic Chem.*, **1969**, **17**, p. 23.