[27] *N. Yanaihara, T. Hashimoto, C. Yanaihara, K. Tsuji, Y. Kenmochi, F. Ashizawa, T. Kaneko, H. Oka, S. Saito, A. Arimura & A. V. Schally,* Biochem. biophys. Res. Commun. *52*, 64 (1973).
[28] *D. H. Coy, E. J. Coy & A. V. Schally,* J. med. Chemistry *16*, 83 (1973).
[29] *M. Monahan, J. Rivier, W. Vale, N. Ling, G. Grant, M. Amoss, R. Guillemin, R. Burgus, E. Nicolaides & M. Rebstock,* 'Chemistry and Biology of Peptides', J. Meienhofer ed., p. 601, Ann Arbor, Science Publishers, Ann Arbor, 1972.
[30] *J. Chang, R. H. Williams, A. J. Humphries, N. G. Johansson & K. Folkers,* Biochem. biophys. Res. Commun. *47*, 727 (1972).
[31] *C. I. Bliss,* 'The Statistics of Bioassay', Academic Press Inc., New York, 1952.
[32] *B. Kerdelhué, A. Bérault, C. Courte & M. Jutisz,* C. R. hebd. Seances Acad. Sci. (Paris) Ser. D. *269*, 2413 (1969).
[33] *B. Kerdelhué, G. Kann & M. Jutisz,* 'Hormones Glycoprotéiques' Colloque INSERM, M. Jutisz ed., p. 177, published by INSERM, Paris, 1972.
[34] *B. Kerdelhué & M. Jutisz,* Abstr. IVth Int. Congr. Endocrinol. Washington D.C., Excerpta Medica I.C.S. *256*, 141 (1972), (Abstr. No. 352).
[35] *D. H. Spackman, W. H. Stein & S. Moore,* Analyt. Chemistry *30*, 1190 (1958).
[36] *T. Y. Lin & Y. H. Chang,* J. biol. Chemistry *246*, 2842 (1971).
[37] IUPAC-IUB Commission, Biochemistry *5*, 2485 (1966); ibid. *6*, 362 (1967).
[38] *P. Karrer, M. Gisler, E. Horlacher, F. Locher, W. Mäder & H. Thomann,* Helv. *5*, 482 (1922).
[39] *W. Siedel, K. Sturm & R. Geiger,* Chem. Ber. *96*, 1436 (1963).
[40] *E. Kliegler & H. Gibian,* Liebigs Ann. Chem. *649*, 183 (1961).
[41] *W. R. Gray,* 'Methods in Enzymology', C.H.W. Hirs ed., Vol. XI, 139, Academic Press, New York, 1967.
[42] *E. Waser & E. Brauchli,* Helv. *7*, 740 (1924).
[43] *M. Bergmann & L. Zervas,* Chem. Ber. *65*, 1192 (1932).

233. Dicationic Diolefinic Complexes of Palladium(II) and Platinum(II)

Preliminary communication

by **Raymond Roulet** and **Raymond Vouillamoz**

Institut de chimie minérale et analytique de l'Université, 3, Place du Château, 1005 Lausanne

(12. IX. 74)

Uncharged diolefinic complexes M(diolefin)Cl_2 (**1**; M = Pt(II), Pd(II)) have been obtained by *Chatt et al.* in 1957 [1]. The coordinated diolefins are susceptible of nucleophilic attack by alcohols, amines, etc. [1–4]. In view of obtaining complexes in which the double bond is prone to be attacked by weaker nucleophiles and to give thermally 'forbidden' [2+2]-cycloadditions, we have prepared the dicationic complexes [M(diolefin)$(CH_3CN)_2$]$(PF_6)_2$ (**2**; diolefin = cycloocta-1,5-diene, 2,5-norbornadiene) and [Pd(cod)L]$(PF_6)_2$ (**3**; L = 2,2'-dipyridyl, bis(1,2-diphenylphosphine)-ethane).

The white complexes **2** are obtained in the solid state by adding a stoichiometric amount of [Ag$(CH_3CN)_2$]PF_6 to a dichloromethane solution of **1** at $-15°$, extracting **2** from AgCl with acetone and adding acetonitrile then dichloromethane. These complexes are stable when stored at $-15°$. IR.-spectra show that acetonitrile is coordinated (ν(CN) = 2328–2340 cm^{-1}, compared to 2266 for free CH_3CN and 2347

for $Pd(CH_3CN)_4^{2+}$ [5]); ν(CC) and δ(CH) are about the same as those of complexes **1**. ^{1}H-NMR.-spectra show a deshielding of olefinic protons compared to those in the corresponding complexes **1**. Complexes **2** with dicyclopentadiene are more soluble and nucleophilic addition of acetonitrile on the coordinated nitrile occured prior to isolation. IR.- and ^{1}H-NMR.-spectra indicate that the corresponding dicationic imino compounds are formed (ν(NH) = 3360 cm^{-1}, ν(C=N) = 1638 cm^{-1}).

Complexes **2**, for example with cyclooctadiene, react with methanol or *t*-butylalcohol to give the 2-alkoxycyclooct-5-enyl derivatives. Complex **3** (M = Pd, L = 2,2'-dipyridyl) reacts with methanol in the presence of sodium carbonate to give metallic Pd and 1- and 2-methoxycyclocta-1,3-dienes. Thus, as the four sites of coordination of **3** are occupied by ligands not displaced by CH_3OH (or CH_3O^-), we conclude that the nucleophilic attack occurs directly at the coordinated olefin.

Complexes **2**, having two weakly coordinated ligands in *cis*-positions to the diene which is activated by the high positive charge on the metal, could promote cycloadditions with olefins. Indeed $[Pd(nbd)(CH_3CN)_2](PF_6)_2$ in acetonitrile reacts with excess of propylene at $-15°$. The mass- and ^{1}H-NMR.-spectra of the isolated organic product extracted with pentane show that [2+2]- and [2+4]-cycloadditions of propylene on norbornadiene occurred without dimerization of norbornadiene itself. The product of one thermally 'forbidden' [2+2]-cycloaddition, 3-methyltricyclo-[4.2.1.$0^{2,5}$]nonene-7, formed 55% of the extract. The remaining components were mainly the dimers (~30%) and trimers (~10%), 3,8 or 9-dimethyltetracyclo-[4.4.1.$0^{2,5}$.$0^{7,10}$]undecane, 6,10 or 11-dimethyltetracyclo[6.3.0.$0^{2,9}$.$0^{4,8}$]undecane, trimethylpentacyclo[6.4.1.$0^{2,7}$.$0^{3,6}$.$0^{9,12}$]tridecane and trimethylpentacyclo[8.3.0.$0^{2,11}$.-$0^{4,10}$.$0^{6,9}$]tridecane. We did not observe any reaction of complexes **2** with acetylene or acetylene-dimethylcarboxylate.

We are gratcful to Prof. *P. Vogel* for helpful discussions and to the *Fonds national suisse de la recherche scientifique* for a grant (2829.73).

REFERENCES

[1] *J. Chatt, L. M. Vallarino & L. M. Venanzi*, J. chem. Soc. *1957*, 3413.
[2] *R. G. Schultz*, J. Organometal. Chemistry *6*, 435 (1966).
[3] *J. K. Stille & R. A. Morgan*, J. Amer. chem. Soc. *88*, 5135 (1966).
[4] *F. R. Hartley*, 'The Chemistry of Platinum and Palladium', Applied Science Publishers Ltd., London, 1973, p. 386.
[5] *B. B. Wayland & R. F. Schramm*, Inorg. Chemistry *8*, 971 (1969).