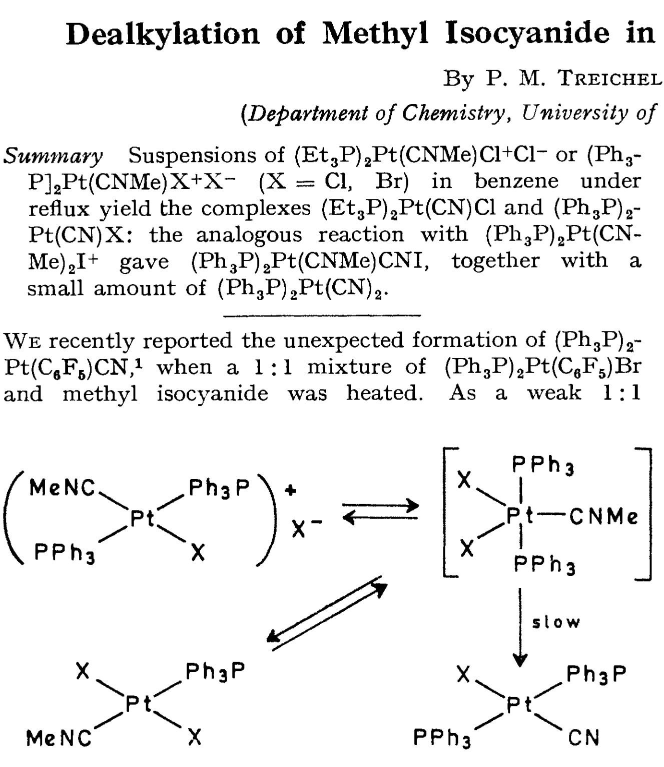
Dealkylation of Methyl Isocyanide in Platinum Complexes of this Ligand

By P. M. TREICHEL* and R. W. HESS

(*Department of Chemistry, University of Wisconsin, Madison, Wisconsin* 53706)

Summary Suspensions of $(Et_3P)_2Pt(CNMe)Cl^+Cl^-$ or $[Ph_3P]_2Pt(CNMe)X^+X^-$ (X = Cl, Br) in benzene under reflux yield the complexes $(Et_3P)_2Pt(CN)Cl$ and $(Ph_3P)_2Pt(CN)X$: the analogous reaction with $(Ph_3P)_2Pt(CNMe)_2I^+$ gave $(Ph_3P)_2Pt(CNMe)CNI$, together with a small amount of $(Ph_3P)_2Pt(CN)_2$.

WE recently reported the unexpected formation of $(Ph_3P)_2Pt(C_6F_5)CN$,[1] when a 1 : 1 mixture of $(Ph_3P)_2Pt(C_6F_5)Br$ and methyl isocyanide was heated. As a weak 1 : 1 complex is formed between these reagents, we suspected that there was an intermediate in this reaction. Previously, in a reaction of C_6F_5Li and $C_5H_5Fe(CO)_2CNMe^+$, $C_5H_5Fe(CO)_2CN$ had been observed as a minor and unexplained product,[2] and in some very early work, $Fe(CNMe)_6{}^{2+}2Cl^-$ was reported to rearrange to $Fe(CNMe)_4(CN)_2$ on being heated under reduced pressure.[3] We now report further on this dealkylation reaction.



We prepared the complexes $(Et_3P)_2Pt(CNMe)Cl^+Cl^-$ and $(Ph_3P)_2Pt(CNMe)Br^+Br^-$ by direct reaction of methyl isocyanide and bisphosphineplatinum dihalide in benzene. An analogous reaction of $(Ph_3P)_2PtI_2$ and methyl isocyanide gave the five-co-ordinate adduct $(Ph_3P)_2Pt(CNMe)_2I^+I^-$, which is also formed by iodide addition to $(Ph_3P)_2Pt(CNMe)^{2+}$. The complex $(Ph_3P)_2Pt(CNMe)Cl^+Cl^-$ could be prepared from this reaction in acetone (but not in benzene or chloroform†). All four complexes have conductivities in acetonitrile representative of 1 : 1 electrolytes. When each is heated under reflux in benzene, elimination of one mole of methyl halide occurs, giving a metal cyanide complex:

$(Et_3P)_2Pt(CN)Cl$, white crystals, m.p. 146—149°, 50%;
$(Ph_3P)_2Pt(CN)Br$, white crystals, m.p. >340°, 82%;
$(Ph_3P)_2Pt(CN)Cl$, white crystals, m.p. 325—330°, 36%;
$(Ph_3P)_2Pt(CNMe)CNI$, yellow crystals, which become colourless at 165—170°, m.p. 328—332°, 70%. A small amount of $(Ph_3P)_2Pt(CN)_2$ accompanied the last complex. The conductivity of $(Ph_3P)_2Pt(CNMe)CNI$ in acetonitrile is approximately one-half of that expected for a 1 : 1 electrolyte.

This dealkylation reaction is the reverse of the well-known alkylation of metal cyanides which gives metal isocyanide complexes.[5] A mechanism can be suggested

---

† On dissolution in chloroform $(Ph_3P)_2Pt(CNMe)Cl^+Cl^-$ rearranges with loss of phosphine to give covalent $(Ph_3P)Pt(CNMe)Cl_2$; this is also the product isolated when the reaction is carried out in benzene. The four-co-ordinate cationic complexes have been reported previously as perchlorate salts in these reactions when the halogen acceptor $NaClO_4$ is added.[4]

involving initial halide attack at the metal with formation of a five-co-ordinate intermediate [six-co-ordinate for the $(Ph_3P)_2Pt(CNMe)_2I_2$] which exists in equilibrium with $(Ph_3P)Pt(CNMe)X_2$. This intermediate, in turn, could eliminate methyl halide to give the observed product.

We acknowledge support from the National Science Foundation through grants and through an NSF Traineeship to R.W.H.

(*Received, September 28th,* 1970; *Com.* 1656.)

[1] P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, 1970, **92**, 4731.
[2] P. M. Treichel and J. P. Stenson, *Inorg. Chem.*, 1969, **8**, 2563.
[3] E. G. J. Hartley, *J. Chem. Soc.*, 1910, 1725.
[4] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074.
[5] L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, New York, 1969.