

Preliminary communication

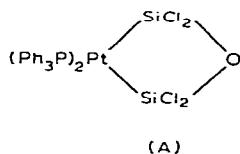
The reaction of hexachlorodisilane with transition metal complexes

F. GLOCKLING and R.E. HOUSTON

Department of Chemistry, The Queen's University, Belfast BT9 5AG (Ireland)

(Received January 13th, 1973)

Schmid and Balk¹ reported, and we confirm, that Si_2Cl_6 adds oxidatively to $\text{Pt}(\text{PPh}_3)_4$ forming $\text{Pt}(\text{PPh}_3)_2(\text{SiCl}_3)_2$ (I). However, whereas they claimed that (I) is dechlorinated by PPh_3 to yield a novel silylene complex $\text{Pt}(\text{PPh}_3)_2(\text{SiCl}_2)_2$ (II) together with PCl_2Ph_3 , we find that if water is rigorously excluded no reaction occurs. In our hands the compound, said to be PCl_2Ph_3 on the basis of its Cl content (found, 20.58%), is unreacted (I) with Cl = 21.6%. Heating (I) and PPh_3 under the prescribed conditions led to a 95% recovery of both reactants. If a trace of water was deliberately introduced this reaction seemed to proceed according to Schmid's description, producing a yellow solution and a yellow solid (after separating from unreacted (I)). This yellow solid is evidently the "silylene complex" which showed strong IR bands at 825 and 608 cm^{-1} (assigned¹ as anomalous $\nu(\text{SiCl})$ vibrations), but a strong broad band was present between 1100–1000 cm^{-1} , indicative of $\nu(\text{SiO})$. It seems to us that this yellow "silylene" is more probably an impure partial hydrolysis product such as (A), and this corresponds closely to the reported analysis*. Schmid also reported that (II) combines with Ph_2C_2 to give



a 5-membered heterocyclic ring, but we observed no reaction between (I), PPh_3 and Ph_2C_2 in boiling benzene.

Other low oxidation state transition metal complexes react with Si_2Cl_6 . Thus $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2$ forms the known compound, $\text{Mo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)\text{SiCl}_3$, m.p. 148°, in 33% yield. Similarly $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ combined with excess Si_2Cl_6 in refluxing benzene without loss of CO yielding $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\text{SiCl}_3)_2$ as a buff solid (found:

*Ref. 1 also reports the bromide $\text{Pt}(\text{PPh}_3)_2(\text{SiBr}_3)_2$ as having: Br found 12.72; calcd. 12.7%. In fact the correct calculated value is 38.2%.

Cl, 23.4; calcd.: 23.7%). Its mass spectrum contained an ion at 1013 a.m.u. with the correct isotope pattern for (parent -Cl). This complex is quite soluble in benzene and extremely readily hydrolysed, when it is converted into $\text{Ir}(\text{Cl})_2(\text{CO})(\text{H})(\text{PPh}_3)_2$. Its IR spectrum contained two bands in the $\nu(\text{C}\equiv\text{O})$ region (2098, 1992 cm^{-1} in C_6H_6), hence it is probably a mixture of isomers. The related rhodium complex $\text{RhCl}(\text{PPh}_3)_3$ combined with excess Si_2Cl_6 forming an orange solid, of empirical formula $\text{Rh}(\text{PPh}_3)\text{SiCl}_2$.

Iron pentacarbonyl and excess Si_2Cl_6 over 10 days at 60° gave CO and the known yellow compound $[(\text{CO})_4\text{FeSiCl}_2]_2$. Its mass spectrum is of interest in that 60% of the ion current is carried by Fe_2Si_2 species, the parent ion being 0.5% abundant. This cyclic compound is presumably formed by reaction between $\text{Fe}(\text{CO})_4(\text{SiCl}_3)_2$ and $\text{Fe}(\text{CO})_5^2$.

REFERENCES

- 1 G. Schmid and H.J. Balk, *Chem. Ber.*, 103 (1970) 2240.
- 2 R. Kummer and W.A.G. Graham, *Inorg. Chem.*, 7 (1968) 1208.