Binuclear Nitric Oxide Complexes of Palladium and Platinum

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TETRAKIS(TRIPHENYLPHOSPHINE)-PALLADIUM(0) (I),[1] and -PLATINUM(0), (II),[2] are known to react with sulphur dioxide to give $Pd(PPh)_3SO_2$,[3] $Pt(PPh_3)_3SO_2$,[3] and $Pt(PPh_3)_2(SO_2)_2$.[4] I now report some preliminary investigations on the reactions of the compounds (I) and (II) with nitric oxide.

Compounds (I) and (II) in benzene solution react with gaseous nitric oxide to give complexes with the empirical formulae

$[Pd(PPh_3)_2NO]_x$, m.p. 208 decomp., and

$[Pt(PPh_3)_2NO]_z$, m.p. 248 decomp.

Both the palladium and platinum complexes were found to be diamagnetic, and this suggests a dimeric formulation with one metal–metal bond, of the type

$$(NO)(Ph_3P)_2M\text{–}M(PPh_3)_2(NO)\ (M=Pd \text{ or } Pt).$$

The dimeric formulation was also confirmed by molecular-weight determinations in benzene solutions.

In view of the fact that these compounds contain NO groups of the low-frequency type, ν_{NO} for the palladium complex 1320 cm.$^{-1}$, and ν_{NO} for the platinum complex 1328 cm.$^{-1}$, the most probable mechanism of their formation seems to be:

$$2M(PPh_3)_4 \rightleftharpoons 2M(PPh_3)_2 + 2PPh_3$$

$$2M(PPh_3)_2 + 2NO \rightarrow 2\cdot M(NO)(PPh_3)_2$$

$$2\cdot M(NO)(PPh_3)_2 \rightarrow (Ph_3P)_2(NO)M\text{–}M(NO)(PPh_3)_2$$

Metal–metal bonds are known to be cleaved by halogens, and spectrophotometric titrations of these complexes, in benzene solution, with bromine showed an end-point at a molar ratio 1 : 1 for both complexes.

In this case the metal–metal bond (Pd–Pd and Pt–Pt) was also found to be cleaved with mercuric halides, reacting at a molar ratio 1 : 1, possibly according to the equation

$$(Ph_3P)_2(NO)M\text{–}M(NO)(PPh_3)_2 + HgX_2 \downarrow (Ph_3P)_2(NO)M\text{–}HgX + (Ph_3P)_2(NO)MX$$

a reaction which is further being investigated with the aim of preparing complexes containing palladium–mercury bonds analogous to the respective platinum complexes, which have been prepared by a different method,[4] and which I found not applicable in the case of palladium.

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