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**PRELIMINARY COMMUNICATION**

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# *sym*-TRINITROBENZENEBIS(TRIPHENYLPHOSPHINE)PLATINUM

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A number of complexes are known containing a bis(triphenylphosphine)platinum entity coordinated to an unsaturated molecule such as diphenylacetylene[1], carbon disulphide[2] or tetracyanoethylene[3]. Although these complexes can be thought of as derivatives of zero-valent platinum, X-ray diffraction studies show that the molecular structures approximate the planar stereochemistry normally associated with complexes of platinum(II). Thus, although the question of oxidation states has not, in fact, been satisfactorily settles, the metal atom in these complexes may be considered to be oxidized by the unsaturated ligand.

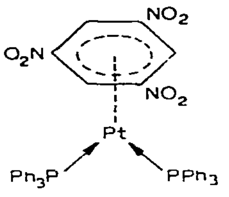
The similarity of 1,3,5-trinitrobenzene (TNB) to tetracyanoethylene as an acceptor in a variety of charge-transfer complexes[4 5] suggested that the former might also act as an acceptor towards tris(triphenylphosphine)platinum(0)[6]. It has subsequently been found that benzene solutions of the TNB and $Pt(PPh_3)_3$ (3:1 molar ratio) darken rapidly, and on refluxing for 1.5 hours under nitrogen, deposit fine, black needle-like crystals which analyze as $Pt(TNB)(PPh_3)_2$ (A), m.p. 200–201°. (Found: C, 53.41; H, 3.83; N, 4.38 mol.wt. ($CHCl_3$), 1080. $C_{42}H_{33}N_3O_9P_2Pt$ calcd.: C, 54.08; H, 3.57; N, 4.50; mol.wt., 933.) The monomeric complex is slightly soluble in chloroform and dichloromethane, but is insoluble in ethyl ether, alcohol and benzene. Attempts to recrystallize the complex from $CH_2Cl_2/CH_3OH$ or $CH_2Cl_2/Et_2O$ yielded black, needle-like crystals which had the same appearance and infrared spectrum as the crude material. However, whereas A appears to be indefinitely stable in the solid state, the recrystallized complex is air-sensitive, yielding a brown material (B) over a period of three days.

As well as bands which may be assigned to triphenylphosphine, the infrared spectrum of A (nujol mull) contains bands at 1615 m, 1520 s and 1340 s $cm^{-1}$ which may be assigned to $\nu$(C=C), $\nu(NO_2)$ *(asym)* and $\nu(NO_2)$ *(sym)*, respectively[7]. There are also medium intensity bands at 965 and 820 $cm^{-1}$, which may be assigned to C–N stretching modes.

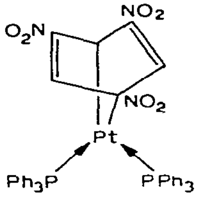
The NMR spectrum ($CDCl_3$) contains a complex multiplet in the region 2.0–3.4 $\tau$, which may be assigned to the thirty phenyl protons, and two weak, broad lines at 3.55 $\tau$ and 8.47 $\tau$ which may be assigned to the olefinic and aliphatic protons, respectively, of structure II. The latter two lines are probably broadened by spin–spin coupling with $^{195}Pt$ and $^{31}P$. Satisfactory integration of the spectrum could not be achieved because of the low solubility of the complex. The complex is also rather unstable in solution, and the spectrum slowly changes with time.

In the infraredspectrum of B, the C=C stretch at 1615 $cm^{-1}$ disappears, while the N=O stretching bands shift to 1542 $cm^{-1}$ and 1382 $cm^{-1}$. In addition, a strong, complex multiplet appears in the region 1100–1200 $cm^{-1}$. The latter bands may indicate P=O or C–O stretching vibrations.

Two structures appear to be possible for A, a symmetric $\pi$-arene structure, I, or a 1,4-$\sigma$-bonded cyclohexadienyl structure, II. The oxidation states of the platinum would be 0 and +2, respectively.



(I)



(II)

Structure I seems unlikely since it violates the rare-gas rule. Furthermore, the $\pi$-arene group should be susceptible to displacement by strong nucleophiles, and it has been found that refluxing chloroform solutions of A and tetraphenylarsonium cyanide do not give the deep red colour which is characteristic of the cyanide ion - TNB Meisenheimer-type complex[8].

Structure II is very similar to that found for $\pi$-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium[9]. Although the infrared spectrum of A is very similar to that of free, planar TNB, it can also be interpreted in terms of structure II, in which the C=C and N=O bonds are largely conjugated[7b]. If the formation of B, then, involves oxidation of the C–C double bonds, as seems likely from the infrared spectrum, the $NO_2$ groups would no longer be conjugated. Therefore the N=O stretching bands should increase in frequency[7] as is observed.

The black colour of A is due to broad absorptions at about 5400 and 4180 m$\mu$, which are shoulders on a much more intense charge-transfer band at higher energy. The electronic and vibrational spectra are virtually identical in the solid state and in solution, and hence the intense colour cannot be due to intermolecular interactions.

It is interesting to note that whereas electron withdrawing groups on the arene ring tend to destabilize $\pi$-arene complexes of the earlier transition metals, *i.e.* of chromium, molybdenum and tungsten[10], electron-withdrawing groups appear to stabilize the $\sigma$-bonded arene complexes of the later transition metals. No complexes could be isolated from reactions of $Pt(PPh_3)_3$ with 2,4,6-trinitrotoluene, *m*-dinitrobenzene or benzene. Picryl chloride gave the chloropicryl compound $PtCl[C_6H_2(NO_2)_3][PPh_3]_2$, which is being investigated further.

## ACKNOWLEDGEMENTS

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