Journal of Organometallic Chemistry, 56 (1973) C33–C35
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Preliminary communication

The structure of a four coordinate acyliminoplatinum complex, *trans*-PtI[C(Me)=NC$_6$H$_4$Cl](PEt$_3$)$_2$.

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(Received May 1st, 1973)

SUMMARY

The crystal structure of the isocyanide insertion product *trans*-iodobis(triethylphosphine)(1-*p*-chlorophenylimino)methylplatinum(II) has been determined by X-ray diffraction; it is shown to have a non-bonding Pt—N distance of 3.04 Å; thus the previously suggested pseudo five-coordination geometry for these compounds is incorrect.

Recent studies on the reactions of various isocyanides with -palladium(II) and -platinum(II) derivatives MX(R)(Phos)$_2$, (Phos = various tertiary phosphines, R = alkyl- or aryl-, X = I, Br, Cl), have shown that initial coordination of the isocyanide to the metal occurs, followed by migration of the alkyl group from the metal to the carbon atom of the coordinated isocyanide, resulting overall in the insertion of the isocyanide into the metal—carbon bond[1,2,3]. A similar insertion also occurs during oxidative addition of methyl iodide to Ni(CN-t-Bu)$_4$ or [Pd(CN-t-Bu)$_2$]$_x$[4]. For both the oxidative addition reactions, and for the reactions of PdX(R)(Phos)$_2$ and isocyanides, multiple insertions are noted; these reactions presumably occur in a stepwise manner. In contrast, studies with the platinum(II) complexes show that insertion of only a single isocyanide occurs.

Although the insertion products, MX[CR=NR](Phos)$_2$ (M = Pt, Pd) appear straightforward, an anomaly was noted in the PMR spectra of several compounds. Yamamoto and Yamazaki reported the room temperature non-equivalence of the two phosphine methyl groups in *trans*-PdI[C(Me)=NC$_6$H$_{11}$](PMe$_2$Ph)$_2$[5] (C$_6$H$_{11}$ = cyclohexyl), and later also reported the same effect for the platinum analog[6]. The non-equivalence could be removed by raising the temperature. These data were explained by assuming an additional palladium—isocyanide interaction through the lone pair of electrons on the imino nitrogen atom, making the metal five-coordinate. Since five-coordination is somewhat rare for these metals, we felt that restricted rotation about the metal—carbon bond was the more likely explanation for these data. This view was qualitatively supported in our work by the observation that only the relatively bulky *p*-chlorophenylisocyanide derivatives gave PMR spectra showing the absence of a plane of symmetry in the molecule[2]. As a means of resolving this issue, the determination of the crystal structure of one of these compounds, *trans*-$PtI[C(Me)=NC_6H_4Cl](PEt_3)_2$, was undertaken. Crystals of the complex, prepared previously[2], were recrystallised from dichloromethane/diethyl ether and gave colorless plates suitable for a structure determination.

Crystal data. Crystals of the compound $C_{20}H_{37}ClINP_2Pt$, mol.wt. 710.89, were monoclinic, belonging to the space group $P2_1/c$ with $a = 20.902(3)$, $b = 8.530(1)$, $c = 15.175(1)$Å, $\beta = 107.760(9)^\circ$, D_M 1.828 g·cm^{-3} (by flotation), D_C 1.832 g·cm^{-3} $Z = 4$, $F(000) = 1368$. Three dimensional X-ray intensity data was recorded on a Syntex $P\bar{1}$ four circle computer-controlled diffractometer using Mo-K_α radiation. The 2480 reflections obtained were corrected for Lorentz-polarization effects[7], the polarization term including a correction for the graphite monochrometer, and merged[7], giving a total of 1791 independent observed reflections, all of which were used in the structure determination which was solved by heavy atom techniques[8]. Full matrix least squares refinement using anisotropic thermal parameters for all atoms heavier than nitrogen and isotropic thermal parameters only for C and N, gave $R = 0.038$ after the data had been corrected for absorption and for anomalous dispersion of the platinum and iodine atoms.

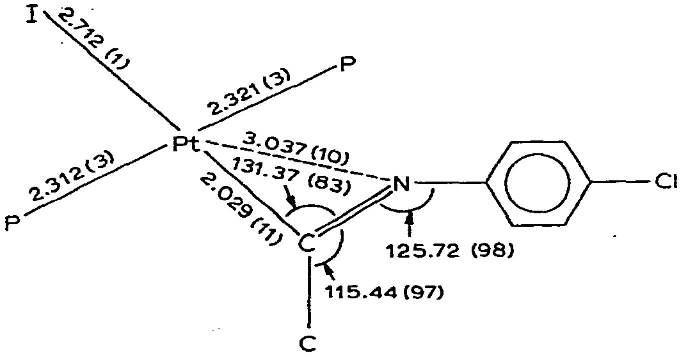

Fig. 1. Principal bond distances (Å) and bond angles (deg.) including standard deviations in *trans*-$PtI[C(Me)=NC_6H_4Cl](PEt_3)_2$. Ethyl groups have been omitted for clarity.

Figure 1 shows the salient features of this structure. The coordination around platinum is essentially square planar with Pt—P distances of 2.312(3) and 2.321(3) Å respectively. The Pt—C distance of 2.029(11) Å is similar to that of 2.020 Å found in *cis*-$PtCl_2[C(OC_2H_5)NHC_6H_5](PEt_3)_2$[9]. The Pt—C=N—C atoms lie in a well-defined plane with the normal at 79.65° to that of the Pt—P_2—I—C plane. The normal to the plane of the benzene ring makes an angle of 36.51° to that of the Pt—C=N—C plane, with the Pt—C—N and C—N—C_6H_4Cl angles of 131.37(83)° and 125.72(98)°, respectively. The nitrogen atom for the imino group, at 3.037(10) Å away from platinum, is clearly not bonded to the metal in this molecular structure as had been suggested earlier. Thus the alternative explanation involving simple restricted rotation of the carbon–metal bond, presumably due to steric factors seems most reasonable.

We are aware that our results and the earlier reported PMR data could be mutually compatible assuming either of two conditions. It is possible, though unlikely in our opinion, that solid and solution structures are different. Secondly, it is also conceivable that the choice of phosphines has caused the structures to be different. Still, one is inclined to accept the simplest and most logical conclusion, that the expected four coordinate geometry is the one found for these species.

Parenthetically, we note that this is the first structure determination of a metal–acylimino complex.

ACKNOWLEDGEMENT

We are pleased to acknowledge support for this work from the UW Graduate School, and from the National Science Foundation through Grant GP 17207. The automated diffractometer equipment was made available in this department from an NSF major instrument grant.

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