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Preliminary communication

Synthesis and structure of chloro(methoxalyl)bis(triphenylphosphine)-palladium

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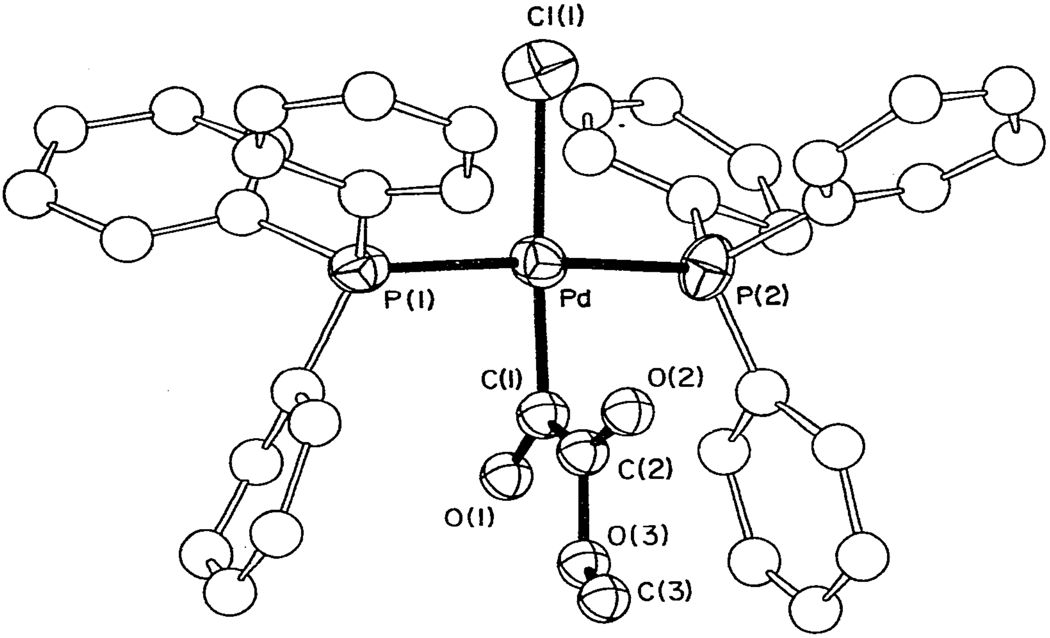
SUMMARY

Palladium(0) and platinum(0) phosphine complexes react with alkoxalyl chlorides (*e.g.*, $ClCOCO_2CH_3$) to yield alkoxalyl complexes. The X-ray structure of one, *trans*-$Pd(Cl)(COCO_2CH_3)[P(C_6H_5)_3]_2$, has been determined. Both the Pt and Pd complexes lose CO to give the corresponding alkoxycarbonyl complexes, $M(Cl)(CO_2CH_3)[P(C_6H_5)_3]_2$.

Both $Pd[P(C_6H_5)_3]_4$ and $Pt[P(C_6H_5)_3]_4$ react with alkoxalyl chlorides ($ClCOCO_2R$ where $R = CH_3$ or C_2H_5) to form the complexes $M(Cl)(COCO_2R)[P(C_6H_5)_3]_2$. They are the first examples of metal complexes containing an alkoxalyl ligand. The complexes exhibit two strong ν(C=O) absorptions in the infrared (*e.g.*, at 1665 and 1720 cm^{-1} for *trans*-$Pd(Cl)(COCO_2CH_3)[P(C_6H_5)_3]_2$ in $CHCl_3$). The lower frequency band is assigned to the carbonyl group adjacent to the metal atom[1]. NMR spectra of the derivatives $M(Cl)(COCO_2CH_3)[P(C_6H_5)_3]_2$ show a methyl singlet at τ6.9.

Yellow crystals of $Pd(Cl)(COCO_2CH_3)[P(C_6H_5)_3]_2 \cdot 0.6CH_2Cl_2$ were obtained by slow evaporation of a CH_2Cl_2/hexane solution containing the complex and twice as many moles of $P(C_6H_5)_3$. Diffractometer measured cell constants for the monoclinic unit cell are: $a = 14.932(9)$, $b = 15.723(5)$ and $c = 17.813(15)$ Å and β 65.2(3)°. There are four molecules of complex in the unit cell which belongs to the common space group $P2_1/c$. Data were collected on a fully-automated Hilger–Watts four-circle diffractometer using Zr-filtered Mo radiation (0.7107Å). A total of 1669 reflections were judged observed after correction for Lorentz, polarization and background effects. All 49 non-hydrogen atoms in the asymmetric unit were easily located using the heavy atom method. Full-matrix, least-squares refinements varying positional and anisotropic thermal parameters for the heavy atoms of the complex, positional and isotropic parameters for the light atoms of the complex and positional and



occupancy parameters for the solvent molecule converged to the present minimum discrepancy index of 0.091.

Figure 1 shows a computer generated drawing of the present X-ray model. The bond distances in the novel methoxyalyl ligand are: Pd—C(1), 1.97(2); C(1)—O(1), 1.19(2); C(1)—C(2), 1.41(4); C(2)—O(2), 1.23(2); C(2)—O(3), 1.46(3); O(3)—C(3), 1.32(3); Pd—O(2), 3.22(2); Pd—Cl, 2.433(6); Pd—P(1), 2.320(7); Pd—P(2), 2.329(6)Å. Bond angles in the ligand are as follows: Pd—C(1)—O(1), 128(2)°; Pd—C(1)—C(2), 113(2)°; O(1)—C(1)—C(2), 118(3)°; C(1)—C(2)—O(2), 135(4)°; C(1)—C(2)—O(3), 121(3); O(2)—C(2)—O(3), 103(3)°; C(2)—O(3)—C(3), 122(3)°.

The Pd—C(1) bond distance is very similar to that observed (1.99Å) for the Pd—C(sp^2) bond of *trans*-$[2\text{-}C_6H_5N{=}NC_6H_4]PdCl[P(C_2H_5)_3]_2$.[2] Like organic oxalyl derivatives such as dimethyloxalate[3] and oxalyl chloride[4], the methoxalyl ligand has an *s-trans* planar conformation. The largest deviation from the least squares plane of the methoxalyl ligand is that of the carbon atom C(3) and is 0.12Å. The least squares plane of the methoxalyl group makes an angle of 93(2)° with the plane formed by Pd, Cl, P(1), and P(2). Thus the molecule as a whole has a pseudo-mirror plane at right angles to the square plane of the complex. The unexpectedly large C(1)—C(2)—O(2) angle and small O(2)—C(2)—O(3) angle appear to result from repulsion between the Pd and O(2).

In $CHCl_3$, CH_2Cl_2, or benzene solution at 25° the *trans*-$Pd(Cl)(COCO_2R)[P(C_6H_5)_3]_2$ complexes readily undergo decarbonylation to give the corresponding *trans* alkoxycarbonyl complexes, $Pd(Cl)(CO_2R)[P(C_6H_5)_3]_2$ [5,6]. However, addition of two moles of $P(C_6H_5)_3$ stabilizes the complexes against decarbonylation indefinitely, allowing crystals of the compound to be grown. The Pt analog, *trans*-$PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ is stable in $CHCl_3$ at 50°, but decarbonylates when refluxed in benzene or when heated to 175° in the solid state. The related pyruvyl complex[7], $CH_3COCOMn(CO)_5$, also decarbonylates slowly.

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