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Preliminary communication

METHYLENE DIOXIME-PALLADIUM(II) COMPLEXES. A "NON-BONDED" Pd···H INTERACTION IN A CHELATING SIX-MEMBERED RING

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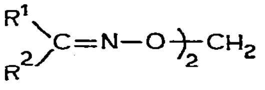
Summary

Treatment of methylene dioximes (I) with palladium(II) chloride gives $[(R^1R^2C{=}NO)_2CH_2]PdCl_2$ (II), their ^{1}H NMR spectra exhibit resonances due to one of the methylene protons in remarkably lower fields (δ 8.99—8.28 ppm). X-ray analysis of IIb ($R^1 = R^2$ = n-Pr) shows that the ligand has boat-like conformation in which the distance between the Pd and the H atom of the OCH_2O-group is 2.46 Å, being much less than expected for the sum of the Van der Waals radii.

Methylene dioximes (I), a previously unknown class of compounds, prepared from ketoximes and dichloromethane [1] are expected to be new bidentate ligands of metal complexes. In an effort to investigate their characteristics as bidentate ligands, we have prepared palladium(II) complexes (II) and found that the ligands have a rarely observed boat-like conformation. Significantly, the preference of this conformation is ascribed to "non-bonded" Pd···H interaction in the chelating six-membered ring of II.

Listed in Table 1 are physical data of complexes II which were prepared by treatment of methylene dioximes (I) with either Na_2PdCl_4 in methanol or $PdCl_2(PhCN)_2$ in benzene at room temperature for 1 h. In the ^{1}H NMR spectra, the methylene proton signals for all complexes II at 0°C show two doublets (*J* 10—11 Hz) around δ 8.5 and 5.5 ppm (Table 1). The former signals, compared with those of the free ligands (I) (δ (Ia) 5.30, δ (Ib) 5.37, δ (Ic) 5.80, and δ (Id) 5.48 ppm) are extremely shifted downfield (Δδ 2.80—3.51 ppm), showing



$(R^1R^2C{=}N{-}O)_2CH_2$

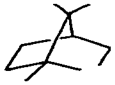
(I)

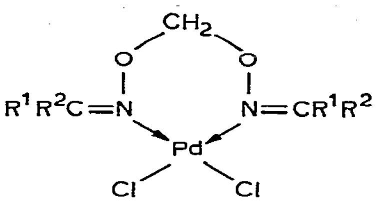
(a) $R^1 = R^2 = CH_3$

(b) $R^1 = R^2 = CH_3CH_2CH_2$

(c) $R^1 = R^2 = PhCH_2$

(d) R^1, R^2 =





(II)

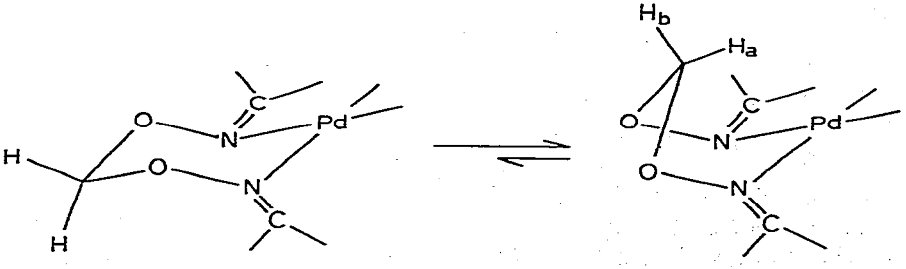
TABLE 1

PHYSICAL DATA AND YIELDS OF IIa—IId

Complex[a]	Yield[b] (%)	M.p. (decomp.) (°C)	IR: ν(C=N)[c] (cm^{-1})	^{1}H NMR[d] $\delta(OCH_2O)$ (ppm)	
				H_a	H_b
IIa	90 (87)	203	1655	8.28 (11)	5.49 (11)
IIb	89	132-133	1630	8.42 (10)	5.48 (10)
IIc	92 (91)	169-170	1600	8.60 (11)	5.72 (11)
IId	92 (58)	169	1655	8.99 (10)	5.41 (10)

[a] Satisfactory elemental analyses were obtained. [b] Yields when Na_2PdCl_4 was used in MeOH; yields when $PdCl_2(PhCN)_2$ was used in benzene are in parentheses. [c] In Nujol. [d] Measured in $CDCl_3$ at 0°C. J (in Hz) in parentheses.

proximity between the hydrogen and the metal [2]. When the temperature is raised, the doublet signals of IIa broaden, coalesce at 48°C, and appear as a broad resonance at 65°C. Complexes IIb and IIc exhibit similar behaviour, but the signals of these complexes do not coalesce even at 65°C*. These results suggest that there is a conformational change between the chair- and boat-like structures (A and B), and structure B, where the Pd atom is close to one of the CH_2 hydrogens (H_a), seems to be preferred at room temperature. To confirm this the structure of IIb was determined by X-ray diffraction.



(A) (B)

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*No significant change is observed in the methylene proton signals of IId between 0 and 65°C, suggesting that complex IId is more conformationally rigid than others. The approximate value of the free energy of activation ($\Delta G^{\ddagger}$) for the conformational change of IIa deduced from the coalescence temperature was 14.7 kcal mol^{-1} (61.7 kJ mol^{-1}).

Crystal data for IIb: $C_{15}H_{30}N_2O_2Cl_2Pd$, $M = 477.7$, monoclinic, space group $P2_1/c$, a 7.197(6), b 16.427(17), c 17.765(9) Å, β 98.70(6)°, $Z = 4$, D_x 1.43 g cm^{-3}, μ(Mo-K_α) 11.4 cm^{-1}. Intensity data for 1365 reflections were collected at room temperature on a Syntex R3 four-circle diffractometer with a graphite-monochromated Mo-K_α radiation source using an ω-scan mode within 2θ less than 50°. The structure was solved by the heavy-atom method combined with the MULTAN method. The hydrogen atoms except those attached to the methyl group were located in a difference map computed after block-diagonal least-squares anisotropic refinement of non-hydrogen atoms. The final refinement was $R = 0.057$, in which all hydrogen atoms were included with fixed parameters.

The geometry around the Pd atom (Fig. 1) is square-planar, as expected the six-membered ring consisting of Pd, N(1), O(1), C(1), O(2), and N(2) atoms is fixed as the boat form. Usually chelate ligands such as 1,3-propanediamine and its derivatives which form six-membered rings prefer to take chair or skew conformation [3] simply because of steric requirements. The preference for boat conformation in our complex is thus a very rare case [4]. The hydrogen atom [H(1)-1] of the CH_2 group is located at 2.46 Å from the metal. This value is much less than that of the sum of the Van der Waals radii of Pd and H atoms, showing the existence of "non-bonded" Pd···H interaction.

A few other organopalladium complexes have been reported to exhibit "non-bonded" interaction of this type. The first observation of this behaviour was

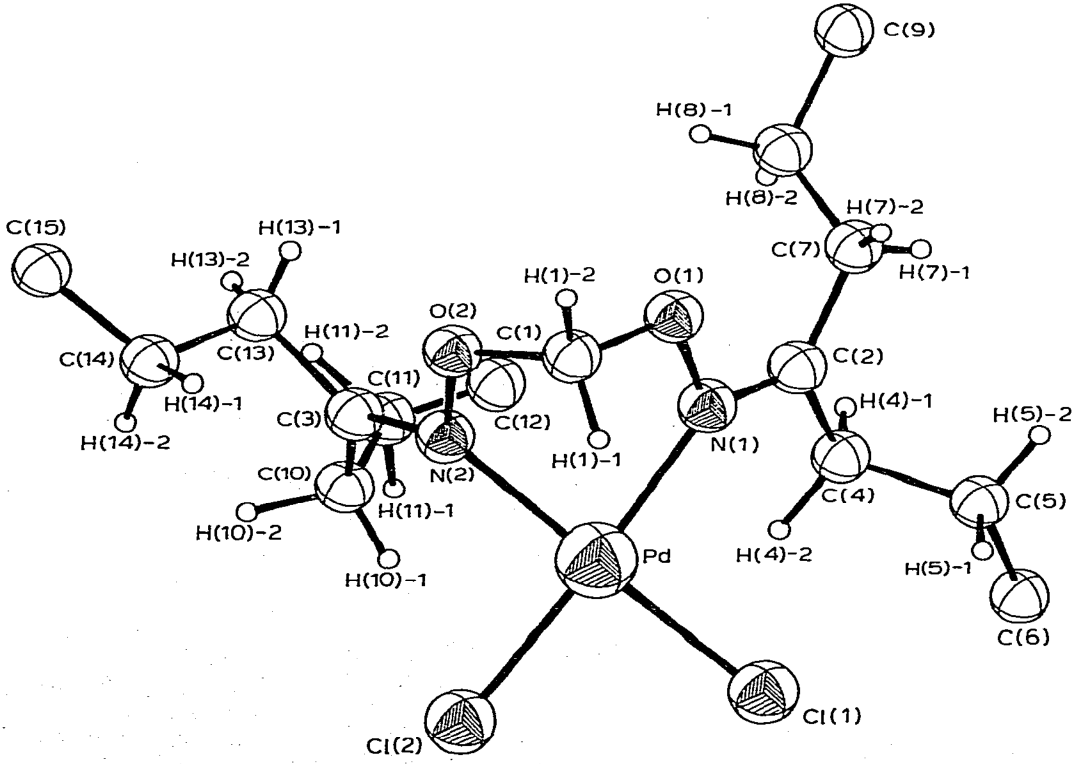

Fig. 1. Structure of compound IIb.

made by Maitlis in the complex *trans*-$Pd(Ph_3P)_2[C_4(CO_2Me)_4H]Br$ where the H atom is approximately over the Pd at ~2.3 Å above the LPdX plane [5]. Another example is the two-coordinated palladium(0) complex, $Pd[PPh(t\text{-}Bu)_2]_2$, in which an attracting interaction between the *ortho*-hydrogen of the phenyl group and the Pd atom has been invoked [6, 7], the Pd···H distance being estimated to be 2.73—2.79 Å. Compared with these values, the distance of 2.46 Å in our complex apparently lies in the range where the attracting interaction of these atoms is exerted, and therefore the observed preference in conformation in our complex is ascribed to this phenomenon.

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