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PRELIMINARY COMMUNICATION

INTRAMOLECULAR REARRANGEMENTS IN PLATINUM-π-TETRAMETHYLALLENE COMPOUNDS AS INFLUENCED BY LIGANDS *trans* TO THE ALLENE GROUP

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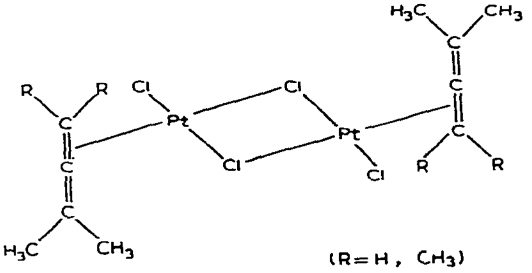
Previously we studied the influence of the electronic properties of various Group V donor ligands L on the movements of the allyl group in the π-allyl complexes $(\pi\text{-}C_3H_5)PdCl(L)$[1] and $L_2Cl_2Rh(\pi\text{-}C_4H_7)$[2] and on the reactions in solution of both π-allyl and diene compounds[3]. A very distinct influence of L on the metal–allyl bond was observed for $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ in which the allyl group is involved in a monomolecular reversible interconversion from the π-allyl into an intermediate σ-allyl species. The activation energy of this process increases with decreasing electron donor properties of the ligands L^2, which are situated *trans* to the π-allyl group[4].

In order to obtain information about the influence of ligands on intramolecular movements of allene groups bonded to metal atoms, we have prepared π-allene compounds of platinum, of which no examples have as yet been reported. They were the orange red dimers $[(TMA)PtCl_2]_2$ and $[(1,1\text{-}DMA)PtCl_2]_2$ and resulted from the reaction of $[\pi\text{-}C_2H_4PtCl_2]_2$[5] with tetramethylallene (TMA) and 1,1-dimethylallene (DMA), respectively. These dimeric compounds were converted into $(TMA)PtCl_2(p\text{-}XC_5H_4N)$ ($X = NH_2, CH_3, C_2H_5$, H, Br, CN) and $(1,1\text{-}DMA)PtCl_2(C_5H_5N)$ by reaction with the appropriate (substituted) pyridine, or by a displacement reaction of $(\pi\text{-}C_2H_4)PtCl_2(pyridine)$[6] with tetramethylallene★.

The molecular configuration of the dimeric compounds is not yet exactly known★★, but NMR and molecular-weight measurements indicate the structure:

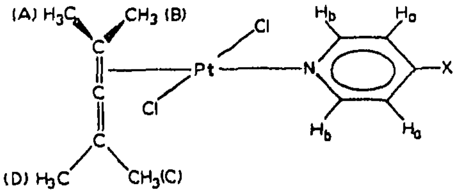


★It is of interest to note that $(\pi\text{-}C_2H_4)PtCl_2(C_5H_5N)$ could only be prepared from Zeise's salt $K[PtCl_3(\pi\text{-}C_2H_4)]$, but not from the dimer $[\pi\text{-}C_2H_4PtCl_2]_2$[7].

★★The crystal structure is presently being determined by T.G. Hewitt.

TABLE 1

PROTON CHEMICAL SHIFTS, PLATINUM-PROTON COUPLING CONSTANTS AND REACTION PARAMETERS OF $[\pi\text{-}R_2C_3(CH_3)_2PtCl_2]_2$ (R = H, CH_3) AND OF $\pi\text{-}(CH_3)_2C_3(CH_3)_2PtCl_2(p\text{-}XC_5H_4N)$



X	δ(A) (ppm from TMS) δ(B)	δ(C)	δ(D)	δ(H_b)	δ(H_a)	k(sec^{-1})	k(sec^{-1}) (-46°)	σ_{para}
NH_2	1.84 J[Pt–(A,B)] = 40.0 cps	2.15	2.56	8.40 J(Pt–H_b) = 30.0 cps	6.58	$10^{9.9}$ $e^{-9700/RT}$	~ 5	-0.660
CH_3	1.89 J[Pt–(A,B)] = 42.0 cps	2.18	2.60	8.70 J(Pt–H_b) = 32 cps	7.35	$10^{10.4}$ $e^{-9600/RT}$	16	-0.170
C_2H_5	1.89 J[Pt–(A,B)] = 42.0 cps	2.18	2.61	8.75 J(Pt–H_b) = 32 cps	7.37	$10^{10.2}$ $e^{-9200/RT}$	15	-0.151
H	1.90 J[Pt–(A,B)] = 44.0 cps	2.20	2.61	9.00 J(Pt–H_b) = 32 cps	7.56	$10^{9.8}$ $e^{-8600/RT}$	30	0.000
Br	1.89 J[Pt–(A,B)] = 46.0 cps	2.20	2.60	8.72 J(Pt–H_b) = 32 cps	7.72	$10^{10.0}$ $e^{-8100/RT}$	75	+0.232
CN	1.89 J[Pt–(A,B)] = 44.0 cps	2.18	2.59	9.12	7.88	$10^{9.7}$ $e^{-7800/RT}$	~200	+0.628
$[TMAPtCl_2]_2$	1.48 1.58 J[Pt–(A,B)] = 44–48 cps	2.21	2.72			$10^{8.3}$ $e^{-7300/RT}$	22	
$[1,1\text{-}DMAPtCl_2]_2$	4.04[a] J(Pt–H) = 52.0 cps	2.22	2.62					

[a] Chemical shift of $H_2C{=}C{=}$. The chemical shift of the four equivalent methyl groups of tetramethylallene is 1.62 ppm. The chemical shifts of the 1,1-dimethylallene protons are 1.70 ppm (CH_3) and 4.50 ppm ($H_2C{=}C$).

The methyl groups bonded to the coordinated part of the tetramethylallene group absorb at high field (at -70° in $CDCl_3$), whereas the two remaining methyl groups absorb at lower fields (Table 1). The two high-field absorptions show a coupling with the ^{195}Pt nucleus. The methyl absorptions for the pyridine derivatives are very similar, the only difference being that the methyl groups which are linked to the coordinated part of tetramethylallene now absorb at the same field, because the molecules have a plane of symmetry. In the case of the 1,1-dimethylallene compound the $H_2C{=}C$ part is coordinated to Pt, as is indicated by the chemical shift which is upfield compared to the free allene, by the coupling of the protons ($H_2C{=}$) with the ^{195}Pt nucleus and by the chemical shifts of the methyl groups which appear at similar low fields as the analogous CH_3 groups in $[(TMA)PtCl_2]_2$.

By raising the temperature from –70° to +50° the four methyl absorptions of $[(TMA)PtCl_2]_2$ broadened and coalesced to their weighted mean (2.00 ppm (δ)). This process is monomolecular, as the $Pt{-}CH_3$ coupling is retained, while the rate $1/\tau$ ($= k$ (sec^{-1})) is independent of the concentration. Much the same behaviour was observed for the (substituted) pyridine derivatives. Again the reaction is monomolecular, because in the temperature range studied (-80 to -10°) ^{195}Pt coupling was observed on the methyl groups of the allene and on the ortho protons of the (substituted) pyridine (Table 1), while the reaction rate ($1/\tau$) was independent of the concentration.

In the case of the 1,1-dimethylallene compounds studied no changes in the NMR spectra were noted.

The suggested reaction path of the intramolecular movement is similar to that proposed for π-$(CH_3)_2C_3(CH_3)_2Fe(CO)_4$[8], which involves a moving of the iron atom from one π-orbital of the allene to the other, which are orthogonal to each other. The reaction rates (Table 1) follow a linear Hammett plot with the σ-values of the *para* substituents (Fig.1)★, which are themselves linearly related to the pK values of the

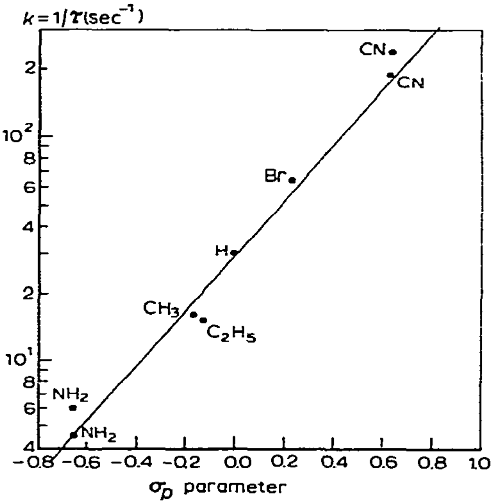


Fig.1

★The two points in Fig. 1 for both X = NH_2 and X = CN indicate the spread in $1/\tau$ values on both ends of the measured range of the Hammett parameter (σ_p) scale.

pyridines[9]. From Fig. 1 it is clear that increasing σ-donor capacity of the ligand strengthens the platinum-π-allene bond★ owing to π-backbonding from the metal to the allene, which results in a decrease in the rate.

It is further clear from the table that the difference between the effects of, for example, CN and NH_2 is not apparent on the CH_3 groups as both the chemical shifts and coupling constant values are little affected.

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★ The increase in Pt-olefin bond strength with increasing back donation is consistent with previous work.