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Preliminary communication

ISOMERISATION IN THE CHEMISTRY OF PLATINACYCLOBUTANE COMPLEXES

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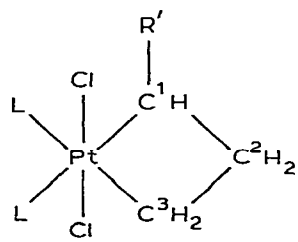
Summary

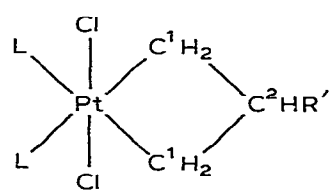
The platinacyclobutane complexes $[PtCl_2L_2(C_3H_5Me)]$, L = pyridine, CD_3CN, or tetrahydrofuran, exist as mixtures of isomers containing $\overline{PtCH_2CHMeCH_2}$ or $\overline{PtCHMeCH_2CH_2}$ groups in rapid equilibrium. Decomposition occurs in some cases to give $[PtCl_2L(CH_3CH_2CH{=}CH_2)]$. Stereospecific skeletal isomerisation also occurs in metallocyclobutanes containing the groups $\overline{PtCHRCHRCH_2} \rightleftharpoons \overline{PtCHRCH_2CHR}$ but, when R = aryl further decomposition gives η-allylplatinum complexes.

Reaction of $[Pt_2Cl_4(C_2H_4)_2]$ with methylcyclopropane gives $\{PtCl_2(C_3H_5Me)\}_4$ which with various ligands, L, gives a mixture of isomeric complexes I and II, R′ = Me, characterised by NMR spectroscopy (Table 1).

The ratio of I/II is strongly dependent on the ligand, L, being 1/5.7, 1/4.0 and 1/2.4 when L = pyridine tetrahydrofuran-d_8 or CD_3CN respectively. Dissolution of the tetramer $\{PtCl_2(C_3H_5)\}_4$ in pyridine-d_5 gave a product mixture of I and II in the ratio 1/3.5. These results show that I and II are in rapid equilibrium. The isomerisation appears to be retarded by excess ligand but is considerably faster than when R′ = Ph [1]. Further, it seems that the position of equilibrium is in-



(I)



(II)

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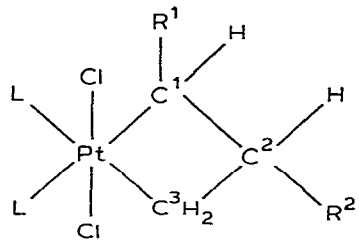
TABLE 1

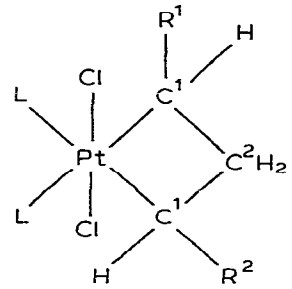
^{1}H AND ^{13}C NMR SPECTRA OF PLATINACYCLOBUTANES, I–IV [c]

Complex				^{1}H NMR [a]				^{13}C NMR [b]					
Type [c]	L	R^1	R^2	$\delta(R^1)$ (ppm)	J(PtH) (Hz)	$\delta(R^2)$ (ppm)	J(PtH) (Hz)	$\delta(C^1)$ (ppm)	J(PtC^1) (Hz)	$\delta(C^2)$ (ppm)	J(PtC^2) (Hz)	$\delta(C^3)$ (ppm)	J(PtC^3) (Hz)
I	C_5H_5N	Me	—	0.84	22	—	—	5.65	—	45.2	—	−8.0	—
II	C_5H_5N	Me	—	1.35	5	—	—	1.0	344	42.6	98	—	—
I	CD_3CN	Me	—	0.70	36	—	—						
II	CD_3CN	Me	—	0.93	4	—	—						
II	C_5H_5N	Bu	—	[d]				−5.2	344	43.4	95		
III	C_5H_5N	Me	Me	1.02	23	1.40	7						
III	C_5H_5N	Ph	Me			0.96	3	16.9	333	41.2	103	−0.2	363.5
III	C_5H_5N	Me	Ph	0.61	24	[d]		10.6	360	57.5	100	−2.9	370
III	t-BuC_5H_4N	Ph	Ph	[d]		[d]		15.1	343	50.6	105	−1.8	377
IV	t-BuC_5H_4N	Ph	Ph	[d]		[d]		6.05	340	41.2	130		
III	t-BuC_5H_4N	4-MeC_6H_4	4-MeC_6H_4	[d]		[d]		15.7	341	50.5	105	−1.6	383
IV	t-BuC_5H_4N	4-MeC_6H_4	4-MeC_6H_4	[d]		[d]		6.3	338	14.6	125		

[a] Ref. ext. TMS. [b] Ref. int. TMS. [c] For nomenclature see text. [d] Complex.



(III)



(IV)

fluenced largely by steric effects. Thus when R′ = Bu or hexyl [2] none of isomer I can be detected when L = pyridine, and when R′ = Me the ratio I/II decreases with increasing bulk of L.

When L = CD_3CN, R′ = Me, the equilibrium mixture of I and II decomposes to give $[PtCl_2(CD_3CN)(CH_3CH_2CH{=}CH_2)]$ (V), as the only product. This is the product expected by decomposition of isomer I only [3], and its formation is thus explained by the reaction of eq. 1. An analogous reaction occurs much more slowly when L = pyridine, and a similar mechanism is invoked for this and related reactions [4].

$$\text{II} \overset{\text{fast}}{\rightleftharpoons} \text{I} \xrightarrow[-CD_3CN]{\text{slow}} \text{V} \qquad (1)$$

The greater reactivity of I is probably due to greater steric effects than in II. Further evidence that steric effects can influence the reactivity of platinacyclobutanes comes from study of complexes derived from *trans*-1,2-disubstituted cyclopropanes, $C_3H_4R^1R^2$. Thus, when R^1,R^2 = Me,Ph or 4-MeC_6H_4, complexes III and/or IV are obtained (Table 1) but, when R^1, R^2 = 2-$MeOC_6H_4$ or 2,5-$(MeO)_2C_6H_3$, η-allylplatinum complexes are formed instead. When decomposition of platinacyclobutanes occurs it seems that alkyl substituents in the ring favour formation of alkene complexes and aryl substituents favour η-allyl complex formation.

When R^1 = R^2 = 4-MeC_6H_4 and L = 4-t-BuC_5H_4N, isomerisation IV ⇌ III occurs readily without formation of isomeric complexes with mutually *cis*-tolyl groups; thus showing that *cis—trans* isomerism does not accompany skeletal isomerisation.

In summary, this work shows that skeletal isomerisation of platinacyclobutane complexes is a general reaction, that it occurs in a stereospecific manner and that the reactions are important in understanding the general chemistry of platinacyclobutanes. The relevance of these reactions to the mechanism of olefin metathesis has been discussed [1].

References

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