

Binuclear Platinum Complexes with Polymethylene Bridges: a Neighbouring Atom Effect in Oxidative Addition

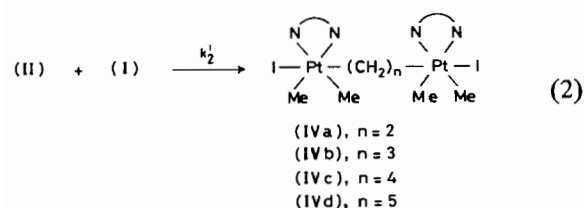
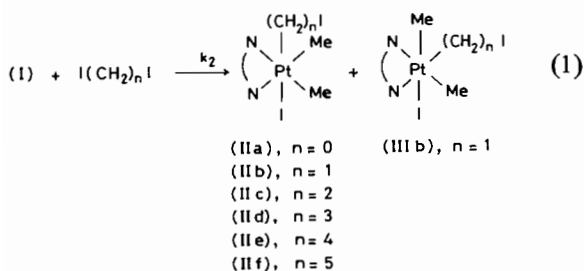
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μ -Methylene and μ -polymethylene complexes of transition elements are of great current interest, for example, as models for intermediates in the Fischer-Tropsch synthesis [1]. One route to such complexes involves reaction of α,ω -dihalogenoalkanes with metal carbonyl anions or with other electron-rich metal centres, and such reactions may lead either to metal derivatives $M(CH_2)_nX$ (M = metal complex, X = halogen) or to $M(CH_2)_nM$ [2–4]. We now report a system, based on oxidative addition to dimethyl-1,10-phenanthrolineplatinum(II),(I), in which both types of complex can be isolated [2]. Kinetic studies now show that the metal atom in $M(CH_2)_nX$ activates the C–X bond to further oxidative addition, and this neighbouring atom effect has been determined quantitatively for the first time for the cases with $n = 3–5$.

The new reactions are shown in eqns. (1) and (2) ($\overline{N\overline{N}} = 1,10$ -phenanthroline).



When $n = 3, 4$ or 5 the reaction of (I) with $I(CH_2)_nI$ in acetone generally gave a mixture of complexes (II) and (IV), which were easily separated since the binuclear derivatives (IV) are very sparingly

soluble in all common organic solvents whereas (II) are soluble in acetone, CH_2Cl_2 or $CHCl_3$. With a large excess of $I(CH_2)_nI$, only (II) was formed and the binuclear complexes (IV) could also be prepared in very high yield from the pure complexes (II) according to eqn. (2). Polymethylene bridged derivatives of platinum were not previously known [5]. When $n = 2$, the products were a mixture of complex (IV a) and ethylene and (II a) rather than the expected (II c); complex (II a) was also formed by reaction of iodine with (I). Finally, when $n = 1$, the products were a mixture of (II b) and (III b) with slow subsequent isomerisation of the *cis* adduct (III b) to the *trans* adduct (II b). Very little or no *cis* oxidative addition was observed in other cases. The compositions of derivatives (II), (III) and (IV) were determined by full elemental analysis and by mass spectrometry, and the stereochemistries of the soluble complexes (II) and (III) were determined by the characteristic 1H NMR spectra [6, 7]. The stereochemistry of (IV), $n = 5$, was determined by 1H and $^{13}C\{^1H\}$ NMR spectroscopy* but, when $n = 2–4$, the complexes were insufficiently soluble for NMR characterization.

Kinetic studies were carried out by monitoring the decay of the MLCT band in the UV-visible spectra due to complex (I) at 473 nm in acetone solution. When $n = 3–5$, the reactions (1) and (2) were first order in both reagents, using conditions in which a large excess of $I(CH_2)_nI$ or complex (II) respectively was used. When $n = 1$, reaction (1) did not follow second order kinetics, but there was an induction period followed by a relatively fast reaction as expected for a free radical chain reaction, and reaction (2) did not occur. When $n = 2$, only an overall rate could be measured using excess $I(CH_2)_2I$; this was first order in each reagent in the early stages of reaction but the kinetics then became more complex. Resulting rate constants are given in Table I, together with comparative data for related alkyl iodides.

The reactivity series ($MeI \gg EtI > PrI \gg IPrI$) and observation of good second order kinetics strongly suggests the S_N2 mechanism of oxidative addition for the *n*-alkyl iodides [8]. The expected low reactivity of CH_2I_2 to nucleophilic attack [9] presumably accounts for it being forced to adopt the free radical mechanism of oxidative addition**, but the low

* 1H NMR (CD_2Cl_2): 1.42 [s, $^2J(PtH)$ 70, MePt]; 0.96 [t, $^3J(HH)$ 7, $^2J(PtH)$ 70, $C^\alpha H_2$]; –0.07 [q, $C^\beta H_2$]; 0.40 [q, $C^\gamma H_2$]. $^{13}C\{^1H\}$ NMR: –5.45 [$^1J(PtC)$ 700, MePt]; 26.40 [$^1J(PtC)$ 670, C^α]; 29.18 [$^2J(PtC)$ 80, C^β]; 30.53 [C^γ].

**It is significant that this was the only reaction to give appreciable *cis* oxidative addition. The mechanistic basis for this effect is under investigation.

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TABLE I. Second Order Rate Constants for Reactions of (I) in Acetone at 25 °C.

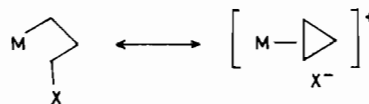
Reagent	$10^3 k_2$ ($\text{l mol}^{-1} \text{s}^{-1}$)	Reagent	$10^3 k'_2$ ($\text{l mol}^{-1} \text{s}^{-1}$)
MeI	$\sim 47,000^a$		
EtI	69		
n-PrI	34		
CH_2I_2	b	(IIb)	~ 0
$\text{ICH}_2\text{CH}_2\text{I}_2$	$\sim 12,000$	(IIc)	c
$\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$	130	(IId)	190
$\text{I}(\text{CH}_2)_4\text{I}$	100	(IIe)	85
$\text{I}(\text{CH}_2)_5\text{I}$	84	(IIf)	88

^aThis reaction was too fast to monitor accurately; this value was determined for $[\text{PtMe}_2(\text{bipy})]$. ^bVery small in early stages (see text). ^cNot measured but must be comparable to the rate constant for $\text{ICH}_2\text{CH}_2\text{I}$ with (I) (see text).

reactivity of (IIb) is almost certainly a result of steric hindrance to attack by (I). Complex (IV) with $n = 1$ and with tetrahedral carbon is not viable due to steric interactions between ligands on the different platinum atoms, but there is good evidence for metal activation of the C–I bond in other iodomethyl derivatives [10]. Overall, rates of both reactions (1) and (2) follow the sequence $n = 2 \gg 3 > 4 \approx 5 \gg 1$. Of particular interest is the observation of a modest neighbouring atom effect when $n = 3-5$. Thus k_2 for reaction (I) with (IId) is $\sim 50\%$ greater than for $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ (corresponding to an increase by a factor of ~ 3 if statistical effects are considered), and 5–6 times greater than for reaction of (I) with n-propyl iodide. The effect is probably much greater for the case with $n = 2$ (Table I) but it could not be measured directly, and it is appreciably lower when $n = 4$ or 5. It will be of great interest to determine the magnitude of the neighbouring atom effect for other metal centres, since a wide variation can be expected.

The commonly observed activation of C–X bonds in derivatives MCH_2X and $\text{MCH}_2\text{CH}_2\text{X}$ may occur by lowering the energy of the transition state by contributions from resonance forms such as $[\text{M} = \text{CH}_2]^+$

X^- or $[\text{MC}_2\text{H}_4]^+\text{X}^-$, and the smaller effect now established for $\text{M}(\text{CH}_2)_3\text{X}$ may then be due to the resonance forms:



thus making displacement of halide easier. Such cyclopropane 'edge-complexes' are commonly proposed in platinum complexes [11], and a similar phenomenon may be important in the Wurtz coupling of 1,3-dihalogenoalkanes to cyclopropanes using zinc metal through the intermediates $\text{XZnCH}_2\text{CH}_2\text{CH}_2\text{X}$ [12].

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