Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK UPON COORDINATED ORGANIC MOIETIES.

XXIII *. ATTACK BY CYCLOHEXYLAMINE UPON THE DIENE LIGANDS IN [MX$_2$(1,5-cyclooctadiene)] (M = Pd, Pt; X = Cl, Br) COMPLEXES
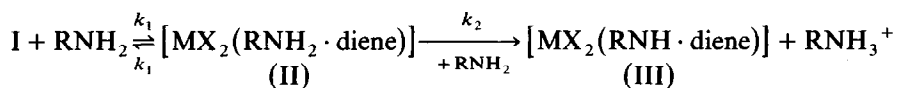
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Summary

Kinetic and spectroscopic studies of the reactions of cyclohexylamine with the complexes [MX$_2$(1,5-cyclooctadiene)] (I) (M = Pd; X = Cl, Br; M = Pt, X = Br) in acetone reveal the rate law, $k_{obs} = K_1 k_2 [\text{amine}]^2$, for the rapid sequence

$$\text{I} + \text{RNH}_2 \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(II)}}{[\text{MX}_2(\text{RNH}_2 \cdot \text{diene})]} \xrightarrow[+\text{RNH}_2]{k_2} \underset{\text{(III)}}{[\text{MX}_2(\text{RNH} \cdot \text{diene})]} + \text{RNH}_3^{+}$$

For X = Br, the palladium(II) complex is ca. 70 times more reactive than its platinum(II) analogue. This is the first quantitative comparison reported to date for nucleophilic attack upon olefins coordinated to Pd^{II} and Pt^{II} centres. The reactivity order Pd$^{II} \gg$ Pt^{II} may arise from the higher ionization potential of Pd^{2+} compared to Pt^{2+}, which makes Pd^{II} a less effective back-π-bonder. Replacing the bromo ligands in [PdBr$_2$(1,5-COD)] by chloro ligands lowers the rate of formation of III by a factor of 8.

The relative abilities of various transition metal centres to activate coordinated π-hydrocarbons towards nucleophilic attack (eq. 1) is a matter of considerable fundamental and industrial significance. In previous papers [1–4], we have explored

$$\text{RML}_n + \text{Nuc} \rightarrow (\text{RNuc})\text{ML}_n \tag{1}$$

this aspect via kinetic studies of type 1 reactions in which the metal is varied down a triad while R, L and Nuc are kept constant. Little dependence of rate on the nature

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* For part XXII see ref. 8.
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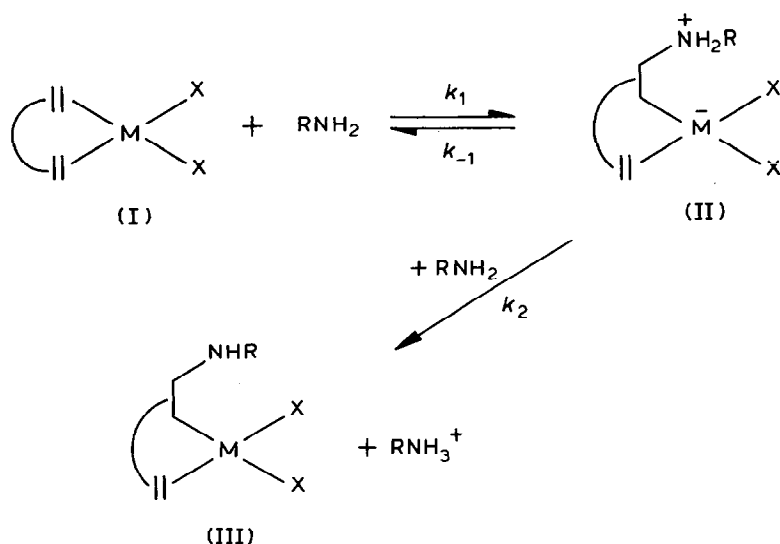
SCHEME 1

of the metal was noted for the chromium [1,2] and manganese [1,3] triads. In contrast, the iron triad metals showed large variations in their ability to activate π-hydrocarbons. For example, for attack by N,N-dimethylaniline on $[M(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ cations, the rate sequence Fe > Os > Ru (41/3.6/1) was observed [4]. We report here kinetic data for the reactions of the compexes $[MX_2(1,5\text{-}cyclooctadiene)]$ (I), (M = Pd, Pt; X = Cl, Br) with cyclohexylamine, which provide the first quantitative comparison of nucleophilic attack on olefins coordinated to palladium(II) and platinum(II) centres.

The complexes undergo rapid reactions with cyclohexylamine in acetone at $0°C$, which could be monitored by visible stopped-flow spectrophotometry utilizing the decrease in absorbance in the region 350–420 nm (except for the M = Pt, X = Cl complex where spectral changes occurred in the UV region). In keeping with earlier studies on related systems [5,6], the sequence shown in Scheme 1 can be assumed, involving reversible formation of the zwitterion II followed by amine-assisted deprotonation to give product III.

The intermediates II (M = Pd, Pt; X-Cl) were isolated by treating $[MCl_2(1,5\text{-}cyclooctadiene]$ (M = Pd, Pt) with an equimolar amount of cyclohexylamine in acetone. The $\nu(N^+\text{-}H)$ and $\delta(N\text{-}H)$ bands observed for species II at 3420–3460 and 1580–1585 cm^{-1}, respectively, are similar to those reported [6] for the analogous complex formed from the reaction of $[PdCl_2(1,5\text{-}hexadiene)]$ with benzylamine. Monomeric structures for II were also confirmed by the absence of bridging $\nu(M\text{-}Cl)$ bands.

Kinetic data at $0°C$ for the reactions I $\rightarrow$ III over a wide range of cyclohexylamine concentrations reveal the general rate law 2. This rate law is consistent with

$$\text{Rate} = k_{obs}[\text{complex}]$$

$$k_{obs} = k[\text{amine}]^2 \tag{2}$$

TABLE 1

RELATIVE REACTIVITIES OF [MX$_2$(1,5-cyclooctadiene)] COMPLEXES TOWARDS CYCLOHE-XYLAMINE IN ACETONE AT 0°C

Complex	K_1k_2 (mol^{-2} dm^6 s^{-1})	Rel. k
[PtBr$_2$(1,5-COD)]	2.68×10^4	1
[PdBr$_2$(1,5-COD)]	1.94×10^6	72
[PdCl$_2$(1,5-COD)]	2.39×10^5	9

the mechanism shown in Scheme 1. Assuming a steady-state concentration for intermediate II, k_{obs} for such a process is given by eq. 3. This simplies to expression 4, in keeping with the observed kinetics, provided $k_{-1} \gg k_2$[amine].

$$k_{obs} = \frac{k_1 k_2 [\text{amine}]^2}{k_{-1} + k_2 [\text{amine}]} \qquad (3)$$

$$k_{obs} = K_1 k_2 [\text{amine}]^2 \qquad (4)$$

Values of K_1k_2 calculated for reactions I → III are summarised in Table 1. Direct comparison of the second-order rate constants (k_1) for addition of cyclohexylamine to the diene ligands in complexes I are not possible. However, comparison of the K_1k_2 values shows that the overall reactivity of 1,5-cyclooctadiene coordinated to palladium(II) is ca. 70 times greater than when coordinated to platinum(II). This is the first time that such a reactivity ratio has been determined. It is consistent with the higher ionization potential of Pd^{2+} compared to Pt^{2+}, suggesting that pal-ladium(II) is a less effective π-back-bonder [7], thus facilitating nucleophilic attack at a coordinated olefin.

Changing the nature of the other ligands attached to the central metal in I also influences the rate of formation of III. Thus, the bromo-palladium substrate is ca. 8 times as reactive as the analogous chloro complex (Table 1).

Each of the above reactions I → III were followed by slower processes, as expected from earlier observations [5] on related systems. These subsequent processes were generally slow enough to follow by conventional spectroscopic techniques, and will be the subject of a subsequent communication.

References

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