

## The Reactivity of Magnesium-Dimethyl and -Diphenyl Towards Platinum(II) Halide Complexes

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*Magnesium-dimethyl and -diphenyl are as reactive as organolithium compounds towards  $PtCl_2L_2$  complexes ( $L = \text{mono-}$  or  $L_2 = \text{bi-dentate tertiary phosphine}$ ) and yield  $PtR_2L_2$  rapidly at  $20^\circ$  in tetrahydrofuran. Evidence is presented for the existence of equilibria between  $PtR_2L_2$  and  $MgR'_2$  or Grignard reagents, and the mixed complex  $PtMePhL_2$  is readily prepared from  $PtClPhL_2$  and  $MgMe_2$ .*

Alkylation and arylation of platinum dihalide complexes  $PtX_2L_2$  have been carried out using organolithium compounds, Grignard reagents<sup>1,2</sup> and diorganomercurials.<sup>3</sup> The highly reactive organolithium compounds, if present in slight excess, yield disubstituted products  $PtR_2L_2$  under mild conditions. By contrast Grignard reagents produce an equilibrium mixture of products, the ratio of which,  $PtR_2L_2:PtRXL_2$ , depends on the nature of L and on the Grignard reagent. For example it decreases in the order  $MgClR > MgBrR \gg MgIR$ , while with aryl Grignard reagents the main product is  $PtR_2L_2$ , possibly because of the greater strength of the platinum-aryl bond or the greater reactivity of aryl-magnesium halides. The effect of L on the position of equilibrium may be illustrated by the reaction between cyclooctadiene platinum diiodide and  $MgI_2Me$  which yields  $PtMe_2(COD)$ <sup>4</sup> whereas with phosphine- or arsine- $PtCl_2$  complexes this reaction gives exclusively  $PtXMeL_2$ . These reactions proceed by direct nucleophilic attack at platinum\* though there is evidence that oxidative addition of  $LiR$  or  $MgXR$  can occur producing a 6-coordinate  $Pt^{IV}$  intermediate.<sup>5</sup> Diorganomercurials are far less reactive towards  $PtX_2L_2$  compounds; after a prolonged period under reflux essentially complete conversion to  $PtXRL_2$  occurs, though only if *cis*- $PtX_2L_2$  is used, *trans* isomers being unreactive. There is some evidence that they proceed predominantly via oxidative addition of  $R-HgR$  to the 4-coordinate platinum complex.<sup>3</sup>

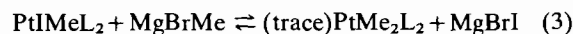
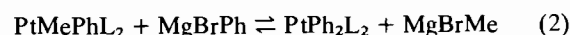
We have investigated the reactions between  $PtCl_2L_2$  and diorgano-magnesium compounds with the object of comparing the reactivity of  $MgR_2$  with Grignard and

organolithium reagents in this type of reaction. Diorganomagnesium compounds, made from the diorganomercurials and magnesium as white powders, are considerably more reactive than the corresponding Grignard reagents and yield  $PtR_2L_2$ . In all cases reactions between *cis* or *trans*- $PtCl_2L_2$  ( $L = PMe_3, PEt_3, PPh_3, L_2 = Ph_2P(CH_2)_n$ ,  $n = 1, 2$ ) and excess  $MgR_2$  ( $R = Me, Ph$ ) proceed to completion within 15 minutes at room temperature in tetrahydrofuran, even though in some cases the phosphine platinum dihalides were insoluble in the solvent. For  $MgMe_2$  it is clearly the first methyl group which is the effective methylating agent. This follows since with slightly less than 2 mol.  $MgMe_2$  the product contained  $PtClMeL_2$ .

These reactions were less satisfactory and somewhat temperamental if the  $MgR_2$  compound was made and used *in situ*, due to the considerably higher temperature necessary for the formation of  $MgR_2$  from the organomercurial and magnesium.<sup>6</sup> Nevertheless both  $HgMe_2$  and  $HgPh_2$  with excess magnesium in refluxing THF or dioxan produce mainly  $PtR_2L_2$  complexes.

Addition of dioxan to Grignard solutions is a standard method for obtaining  $MgR_2$  compounds by displacing the Schlenk equilibrium with precipitation of  $MgCl_2$ <sup>7</sup> but, as applied to  $MgI_2Me$ , the resulting mixture containing  $MgMe_2$  and suspended  $MgI_2(\text{dioxan})_2$  was only slightly more reactive than  $MgI_2Me$  in its reaction with  $PtCl_2L_2$ . If the precipitated  $MgI_2(\text{dioxan})_2$  was separated before addition of the platinum halide complex a higher yield of  $PtMe_2L_2$  was obtained, but again the main product was  $PtImeL_2$ .

The only mixed complexes,  $PtRR'L_2$ , previously reported<sup>8,9</sup> are those in which  $R' = \text{fluorophenyl}$ . We find that the chelating phosphine complex  $PtIme(Ph_2PCH_2PPh_2)$  reacts with  $MgBrPh$  to give a mixture of products (identified mass spectroscopically) consistent with the following equilibria

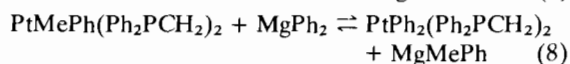
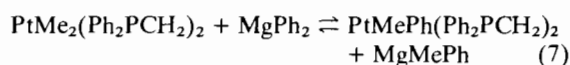


\* Similarly  $MgMe_2$  and  $NiCl(\pi-C_5H_5)(PPh_3)$  combine rapidly at  $0^\circ$  in THF forming  $NiMe(\pi-C_5H_5)(PPh_3)$ .

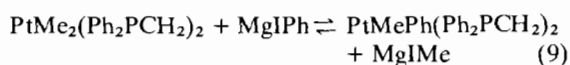
Reactions 1–4 could all proceed via oxidative addition of  $\text{MgXR}$  or  $\text{MgX}_2$  to platinum, but whereas 1, 3 and 4 are generally accepted reaction (2) which involves exchange of Grignard reagents at platinum has not previously been reported. However  $\text{PtPh}_2\text{L}_2$  could be formed by reactions (5) and (6).



In order to determine whether reactions such as (2) occur, we examined halide-free systems of the type  $\text{PtR}_2\text{L}_2 + \text{MgR}'_2$ . The reaction between  $\text{PtMe}_2(\text{Ph}_2\text{PCH}_2)_2$  and excess diphenylmagnesium produced all combinations of products, consistent with equilibria (7) and (8).



Considerable differences in equilibrium constants are implied for reactions of this type, since the reverse processes starting from  $\text{PtPh}_2(\text{Ph}_2\text{PCH}_2)_2$  and excess  $\text{MgMe}_2$  produced the mixed complex  $\text{PtMePh}(\text{Ph}_2\text{PCH}_2)_2$  but gave no evidence for the dimethyl compound,  $\text{PtMe}_2(\text{Ph}_2\text{PCH}_2)_2$ . Reactivity differences between  $\text{MgBrPh}$  and  $\text{MgIPh}$  are implied by the production of platinum diphenyl from  $\text{MgBrPh}$  and  $\text{PtMePhL}_2$  (reaction 2) whereas reaction of  $\text{MgIPh}$  with  $\text{PtMe}_2\text{L}_2$  proceeds only to the stage of the mixed complex (reaction 9).



The related reaction with a monodentate phosphine, *trans*- $\text{PtIme}(\text{PEt}_3)_2 + \text{MgBrPh}$ , proceeded differently in that mass spectroscopic examination of the product gave evidence for  $\text{PtXPh}(\text{PEt}_3)_2$ ,  $\text{PtXMe}(\text{PEt}_3)_2$  and  $\text{PtMe}_2(\text{PEt}_3)_2$  ( $\text{X} = \text{Br}$  and  $\text{I}$ ), with no evidence for the formation of either the mixed complex  $\text{PtMePh}(\text{PEt}_3)_2$  or  $\text{PtPh}_2(\text{PEt}_3)_2$ . This difference is probably a kinetic effect associated with the greater trans effect of phosphorus in labilising the  $\text{Pt-Me}$  and  $\text{Pt-I}$  groups<sup>10</sup> in the case of the chelating phosphine.

The relative reactivities ( $\text{MgPh}_2 > \text{MgMe}_2$ ;  $\text{MgBrPh} > \text{MgIPh}$ ) suggested by this work made it seem likely that the best preparative route to mixed complexes was reaction (10), and this proceeds in 78% yield over 15 minutes at 20°.



## Experimental

All reactions involving air sensitive compounds were carried out under nitrogen, manipulations of organo-

magnesium compounds in the solid phase being accomplished in a glove-box equipped with a recirculatory system ( $\text{N}_2 + \text{H}_2$ ) incorporating an Engelhard Deoxo Dual Puridryer. Mass spectra were obtained at 70 eV using an AEI MS902 and a direct insertion probe. Platinum halide complexes,<sup>11,12</sup> organomercury<sup>13</sup> and organo-magnesium<sup>6</sup> compounds were prepared according to published procedures. Individual experiments in this work were so similar that only illustrative general methods are included. Where mixtures or unsymmetrical products were introduced into a mass spectrometer each produced a clearly defined molecular ion and it was established by the use of known mixtures (eg.  $\text{PtPh}_2\text{L}_2 + \text{PtMe}_2\text{L}_2$ ) that  $\text{PtMePhL}_2$  did not arise by a process occurring within the mass spectrometer.

### Reaction of $\text{PtCl}_2\text{L}_2$ with $\text{MgR}_2$

( $\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PPh}_3$ ;  $\text{L}_2 = (\text{Ph}_2\text{P})_2\text{CH}_2, (\text{Ph}_2\text{PCH}_2)_2$ ;  $\text{R} = \text{Me}, \text{Ph}$ .)

$\text{PtCl}_2\text{L}_2$  (1 mmole) was mixed in the solid phase with  $\text{MgR}_2$  (3 mmole) and tetrahydrofuran (5 ml) added; the resulting suspension was stirred at room temperature until solution was achieved, commonly within 15 min. The ice-cold solution was hydrolysed by the dropwise addition of water and solvent removed under reduced pressure. The residue was extracted with benzene ( $3 \times 10$  ml), the filtrate yielding the requisite diorgano-platinum(II) complex which was further purified utilising published methods.<sup>1,2</sup> The following compounds, all of which gave satisfactory analyses, were prepared in this way: *cis*- $[\text{PtMe}_2(\text{PMe}_3)_2]$  (58%); *cis*- $[\text{PtMe}_2(\text{PEt}_3)_2]$  (78%); *cis*- $[\text{PtMe}_2(\text{PPh}_3)_2]$  (69%);  $\text{PtMe}_2[(\text{Ph}_2\text{P})_2\text{CH}_2]$  (83%);  $\text{PtMe}_2(\text{Ph}_2\text{PCH}_2)_2$  (80%);  $\text{PtPh}_2(\text{PMe}_3)_2$  (64%);  $\text{PtPh}_2(\text{PEt}_3)_2$  (61%);  $\text{PtPh}_2(\text{PPh}_3)_2$  (68%);  $\text{PtPh}_2[(\text{Ph}_2\text{P})_2\text{CH}_2]$  (67%);  $\text{PtPh}_2(\text{Ph}_2\text{PCH}_2)_2$  (73%).

### Reaction of $\text{PtCl}_2\text{L}_2$ with $\text{HgMe}_2$ and $\text{HgPh}_2$ in the presence of magnesium

$\text{PtCl}_2\text{L}_2$  (1 mmole) was stirred with dimethylmercury (3 mmole) and magnesium (5 mmole) in tetrahydrofuran (20 ml) under reflux for several hours. The solution was cooled to room temperature, and hydrolysed by the dropwise addition of water; solvent, along with unreacted dimethylmercury was removed under reduced pressure. The corresponding reactions with  $\text{HgPh}_2$  were carried out in refluxing dioxan (no reaction occurred in THF.) Unreacted  $\text{HgPh}_2$  was removed by sublimation in vacuo. Normal work up gave  $\text{PtR}_2\text{L}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ).

### Methylphenylbis(diphenylphosphino)ethaneplatinum

$\text{PtPh}_2(\text{Ph}_2\text{PCH}_2)_2$  (0.36 g, 0.49 mmole) and mercuric chloride (0.13 g, 0.49 mmole) were refluxed in benzene (10 ml) for 2 hr. Solvent was removed under reduced pressure and  $\text{HgClPh}$  sublimed onto a cold finger.  $\text{MgMe}_2$  (0.27 g, 4.9 mmole) was added to the

residue in THF (10 ml). Normal work-up and crystallisation from benzene/pet. ether (80–100° C) afforded the complex as a white solid, m.p. 197–202° C (78%) (Found: C, 57.73; H, 4.67; C<sub>33</sub>H<sub>32</sub>P<sub>2</sub>Pt requires C, 57.81; H, 4.67%).

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