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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 = mono- or L_2 = bi-dentate tertiary phosphine) and yield PtR_2L_2 rapidly at 20° 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[1,2] and diorganomercurials.[3] 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 arylmagnesium halides. The effect of L on the position of equilibrium may be illustrated by the reaction between cyclooctadiene platinum diiodide and MgIMe which yields $PtMe_2(COD)$[4] 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.[5] 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 predominently via oxidative addition of R–HgR to the 4-coordinate platinum complex.[3]

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 = $Ph_2P(CH_2)_nPPh_2$, 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.[6] 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 $MgCl_2$[7] but, as applied to MgIMe, the resulting mixture containing $MgMe_2$ and suspended $MgI_2(dioxan)_2$ was only slightly more reactive than MgIMe in its reaction with $PtCl_2L_2$. If the precipitated $MgI_2(dioxan)_2$ 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[8,9] are those in which R' = 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

$$PtIMeL_2 + MgBrPh \rightleftarrows PtMePhL_2 + MgBrI \quad (1)$$

$$PtMePhL_2 + MgBrPh \rightleftarrows PtPh_2L_2 + MgBrMe \quad (2)$$

$$PtIMeL_2 + MgBrMe \rightleftarrows (trace)PtMe_2L_2 + MgBrI \quad (3)$$

$$PtPh_2L_2 + MgX_2 \rightleftarrows PtXPhL_2 + MgXPh \quad (4)$$

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* Similarly $MgMe_2$ and $NiCl(\pi\text{-}C_5H_5)(PPh_3)$ combine rapidly at 0° in THF forming $NiMe(\pi\text{-}C_5H_5)(PPh_3)$.

Reactions 1–4 could all proceed via oxidative addition of $MgXR$ or 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 $PtPh_2L_2$ could be formed by reactions (5) and (6).

$$PtMePhL_2 + MgX_2 \rightleftharpoons PtXPhL_2 + MgXMe \qquad (5)$$

$$PtXPhL_2 + MgBrPh \rightleftharpoons PtPh_2L_2 + MgBrX \qquad (6)$$

In order to determine whether reactions such as (2) occur, we examined halide-free systems of the type $PtR_2L_2 + MgR'_2$. The reaction between $PtMe_2(Ph_2PCH_2)_2$ and excess diphenylmagnesium produced all combinations of products, consistent with equilibria (7) and (8).

$$PtMe_2(Ph_2PCH_2)_2 + MgPh_2 \rightleftharpoons PtMePh(Ph_2PCH_2)_2 + MgMePh \qquad (7)$$

$$PtMePh(Ph_2PCH_2)_2 + MgPh_2 \rightleftharpoons PtPh_2(Ph_2PCH_2)_2 + MgMePh \qquad (8)$$

Considerable differences in equilibrium constants are implied for reactions of this type, since the reverse processes starting from $PtPh_2(Ph_2PCH_2)_2$ and excess $MgMe_2$ produced the mixed complex $PtMePh(Ph_2PCH_2)_2$ but gave no evidence for the dimethyl compound, $PtMe_2(Ph_2PCH_2)_2$. Reactivity differences between MgBrPh and MgIPh are implied by the production of platinum diphenyl from MgBrPh and $PtMePhL_2$ (reaction 2) whereas reaction of MgIPn with $PtMe_2L_2$ proceeds only to the stage of the mixed complex (reaction 9).

$$PtMe_2(Ph_2PCH_2)_2 + MgIPh \rightleftharpoons PtMePh(Ph_2PCH_2)_2 + MgIMe \qquad (9)$$

The related reaction with a monodentate phosphine, *trans*-$PtIMe(PEt_3)_2$ + MgBrPh, proceeded differently in that mass spectroscopic examination of the product gave evidence for $PtXPh(PEt_3)_2$, $PtXMe(PEt_3)_2$ and $PtMe_2(PEt_3)_2$ (X = Br and I), with no evidence for the formation of either the mixed complex $PtMePh(PEt_3)_2$ or $PtPh_2(PEt_3)_2$. This difference is probably a kinetic effect associated with the greater trans effect of phosphorus in labilising the Pt–Me and Pt–I groups[10] in the case of the chelating phosphine.

The relative reactivities ($MgPh_2 > MgMe_2$; MgBrPh> 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°.

$$PtClPhL_2 + MgMe_2 \rightleftharpoons PtMePhL_2 + MgClMe \qquad (10)$$

Experimental

All reactions involving air sensitive compounds were carried out under nitrogen, manipulations of organomagnesium compounds in the solid phase being accomplished in a glove-box equipped with a recirculatory system ($N_2 + H_2$) 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,[11,12] organomercury[13] and organo-magnesium[6] 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. $PtPh_2L_2 + PtMe_2L_2$) that $PtMePhL_2^+$ did not arise by a process occurring within the mass spectrometer.

Reaction of $PtCl_2L_2$ with MgR_2

(L = PMe_3, PEt_3, PPh_3; $L_2 = (Ph_2P)_2CH_2$, $(Ph_2PCH_2)_2$; R = Me, Ph.

$PtCl_2L_2$ (1 mmole) was mixed in the solid phase with 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 × 10 ml), the filtrate yielding the requisite diorganoplatinum(II) complex which was further purified utilising published methods.[1,2] The following compounds, all of which gave satisfactory analyses, were prepared in this way: *cis*-$[PtMe_2(PMe_3)_2]$ (58%); *cis*-$[PtMe_2(PEt_3)_2]$ (78%); *cis*-$[PtMe_2(PPh_3)_2]$ (69%); $PtMe_2[(Ph_2P)_2CH_2]$ (83%); $PtMe_2(Ph_2PCH_2)_2$ (80%); $PtPh_2(PMe_3)_2$ (64%); $PtPh_2(PEt_3)_2$ (61%); $PtPh_2(PPh_3)_2$ (68%); $PtPh_2[(Ph_2P)_2CH_2]$ (67%); $PtPh_2(Ph_2PCH_2)_2$ (73%).

Reaction of $PtCl_2L_2$ with $HgMe_2$ and $HgPh_2$ in the presence of magnesium

$PtCl_2L_2$ (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 $HgPh_2$ were carried out in refluxing dioxan (no reaction occurred in THF.) Unreacted $HgPh_2$ was removed by sublimation in vacuo. Normal work up gave PtR_2L_2 (R = Me, Ph).

Methylphenylbis(diphenylphosphino)ethaneplatinum

$PtPh_2(Ph_2PCH_2)_2$ (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 HgClPh sublimed onto a cold finger. $MgMe_2$ (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; $C_{33}H_{32}P_2Pt$ requires C, 57.81; H, 4.67%).

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