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SELECTIVITY IN MULTIPLE METHYLATION OF $MCl_n(PR_3)_m$ COMPOUNDS

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Abstract—Reaction of $RhCl_3L_3$ (L = PMe_2Ph or $PMePh_2$) with excess MeLi or MeMgCl reveals a distinct tendency to stop at the $RhMe_2ClL_3$ stage. This behaviour is attributed to the concentration of all Cl → Rh π-donation into the single remaining metal–halogen bond, and is shown to be a phenomenon of even broader occurrence and greater potential generality. For *cis,mer*-$RhMe_2ClL_3$ containing the bulkier ligand $PMePh_2$, variable temperature ^1H and ^{31}P NMR studies reveal the occurrence of two dynamic processes: hindered rotation about Rh—P and P—C bonds and also dissociation of the unique phosphine *trans* to one methyl group.

We report separately[1] that the reaction of (tripod)$CrCl_3$ (tripod = $MeC(CH_2PMe_2)_3$) with excess *n*-BuLi (6 mol/mol Cr), run under mild conditions to avoid decomposition of the chromium alkyl product, reveals a considerable selectivity to stop at the *di*alkylation stage: (tripod)Cr(*n*-Bu)$_2$Cl. We report here sufficient additional examples of this behaviour to qualify it as a consistent pattern and offer an explanation subject to further experimental test.

EXPERIMENTAL

All manipulations were carried out using standard Schlenk and glove-box techniques under purified nitrogen. Methyl lithium and methyl magnesium chloride solutions were purchased from Aldrich Chemicals, methyldiphenyl phosphine from Strem Chemicals, and chlorine gas from Matheson Gas Company. Benzene, pentane and tetrahydrofuran were dried and distilled prior to use from solutions containing sodium/potassium benzophenone ketyl. ^1H and ^{31}P NMR spectra were recorded on a Nicolet NT-360 spectrometer at 360 and 146 MHz, respectively.

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mer-$RhCl_3(PMe_2Ph)_3$

This was made according to a literature procedure.[2] ^1H NMR (360 MHz, C_6D_6, 25°C): 1.1 ppm (d, PMe, J = 11 Hz), 2.0 ppm (vt, PMe, line spacing = 4.2 Hz), 6.7–7.6 ppm (m, Ph). $^{31}P\{^1H\}$ NMR (146 MHz, C_6D_6, 25°C): 7.3 ppm (d of t, $J_{P—Rh}$ = 113 Hz; $J_{P—P'}$ = 25 Hz); −4.7 ppm (d of d, $J_{P'—Rh}$ = 85 Hz; $J_{P—P'}$ = 25 Hz).

mer-$RhCl_3(PMePh_2)_3$

Into an ethanol slurry of $RhCl_3 \cdot nH_2O$ (1.0 g, 3.8 mmol) was syringed $PMePh_2$ (2.28 g, 11.43 mmol). The solution was then stirred and refluxed for 1 h. Allowing this solution to cool to room temperature yielded large amounts of a yellow–orange precipitate.

This precipitate, a 50:50 mixture of $RhCl_3(PMePh_2)_3$ and $RhHCl_2(PMePh_2)_3$, was collected by filtration and dried *in vacuo*. This mixture was dissolved in CH_2Cl_2 and converted completely to *mer*-$RhCl_3(PMePh_2)_3$ by slow addition of Cl_2 (0.5 cm^3 portions) using a gas-tight syringe. Reaction progress is conveniently monitored by $^{31}P\{^1H\}$ NMR. After complete conversion, the volume of CH_2Cl_2 was reduced to 15 cm^3, the product was precipitated using pentane, and yellow–orange *mer*-$RhCl_3(PMePh_2)_3$ was collected by fil-

tration. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): −3.5 ppm (d of t, $J_{P—Rh}$ = 114 Hz, J_{PP} = 24 Hz); −5.7 ppm (d of d, $J_{P—Rh}$ = 85 Hz).

Reaction of $RhCl_3(PMe_2Ph)_3$ *with* MeMgCl

To $RhCl_3(PMe_2Ph)_3$ (2.75 g) in 50 cm^3 of benzene was added 25 cm^3 of 2.7 M MeMgCl in Et_2O. The volume was reduced *in vacuo* to 50 cm^3 to remove most of the ether, and the solution was refluxed for 3 h. Excess Grignard was hydrolysed by the addition of 10 cm^3 of water and stirring. The benzene layer was separated from the aqueous layer and was retained. The aqueous layer and associated solids were extracted with 2 × 50 cm^3 of CH_2Cl_2. From the dried $(MgSO_4)CH_2Cl_2$ extracts was isolated 0.75 g of colourless $RhMe_3(PMe_2Ph)_3$. ^1H NMR (360 MHz, 25°C, CD_2Cl_2): −0.28 (m, 9H); 1.10 (d, $J_{Me—P}$ = 8 Hz, 18H); 7.0–7.5 (m, Ph—P). $^{31}P\{^1H\}$ NMR (146 MHz, 25°C, C_6D_6): −8.9 (d, $J_{P—Rh}$ = 80 Hz). From the dried benzene phase was isolated 1.25 g of yellow *cis,mer*-$RhMe_2Cl(PMe_2Ph)_3$. ^1H NMR (360 MHz, 25°C, CD_2Cl_2): −0.03 (m, 3H); 0.48 (q, 3H); 0.85 (d, PMe); 1.20 (t, PMe); 1.40 (t, PMe); 7.0–7.5 (m, Ph—P). $^{31}P\{^1H\}$ NMR (146 MHz, 25°C, C_6D_6): −0.1 (d of d, $J_{P—Rh}$ = 110 Hz), −18.0 (d of t, $J_{P—Rh}$ = 83 Hz, $J_{P—P'}$ = 25 Hz).

Reaction of $RhCl_3(PMePh_2)_3$ *with* MeLi

To a homogeneous THF solution of $RhCl_3(PMePh_2)_3$ (0.57 g, 0.7 mmol) was added a diethyl ether solution of MeLi (1.4 M, 12.6 mmol). The solution immediately turned deep red–brown and then gradually lightened over a period of 3 h. At this stage, the solution was cooled to 0°C and the unreacted MeLi was hydrolysed with THF–H_2O (60:40). The volatiles were removed *in vacuo* and the resulting off-white solid was extracted with 60 cm^3 of CH_2Cl_2 and filtered to yield a yellow homogeneous solution. The volume of CH_2Cl_2 was reduced to 15 cm^3 and pentane added to precipitate $RhMe_2Cl(PMePh_2)_3$ as a pale yellow powder. ^1H NMR (360 MHz, −30°C, CD_2Cl_2): −0.55 (m, 3H); 0.23 (br q, line spacing 10 Hz, 3H), 1.27 (d, $J_{P—CH_3}$ = 7 Hz, 3H); 1.9 (br. s, 6H); 7–7.8 (m, P—Ph). ^{31}P (146 MHz, −10°C, CH_2Cl_2): −12.8 (d or t, $J_{P—Rh}$ = 76 Hz, $J_{P—P}$ = 21 Hz); 11.5 (br d, $J_{P—Rh}$ = 110 Hz).

RESULTS

Polyalkylation of $RhCl_3L_3$

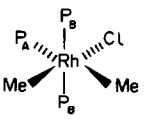
We find that reaction of *mer*-$RhCl_3(PMe_2Ph)_3$ with an excess (15 mol/mol Rh) of MeMgCl in benzene at 80°C gives only a low (28%) yield of the *per*-alkyl compound, $RhMe_3(PMe_2Ph)_3$. The major product is the compound *cis,mer*-$RhClMe_2(PMe_2Ph)_3$, which is easily separated from $RhMe_3(PMe_2Ph)_3$ by its higher solubility in benzene; the trimethyl compound may be dissolved in CH_2Cl_2.

A similar tendency to leave one chloride unreacted is demonstrated by *mer*-$RhCl_3(PMePh_2)_3$, which reacts with 18 mol MeLi/mol Rh in THF in the temperature range 0–25°C to give only *cis,mer*-$RhClMe_2(PMePh_2)_3$. Since $RhClMe_2(PMePh_2)_3$ readily dissociates phosphine in solution (see below), the resistance of the last chloride to alkylation cannot be due to the coordinatively saturated character of this compound. That is, the mechanism in eq. (1) (P = $PMePh_2$) remains available

$$\begin{aligned} RhClMe_2P_3 &\rightleftarrows RhClMe_2P_2 + P \\ RhClMe_2P_2 + MeLi &\rightarrow Li[RhClMe_3P_2] \\ Li[RhClMe_3P_2] &\rightarrow RhMe_3P_2 + LiCl \\ RhMe_3P_2 + P &\rightarrow RhMe_3P_3. \end{aligned} \qquad (1)$$

Solution dynamics of cis,mer-$RhClMe_2(PMePh_2)_3$

This molecule shows two P*Me* ^1H NMR signals at and below 25°C in CD_2Cl_2. At −30°C, there are two Rh/Me signals, one a pseudoquartet and the other an unresolved multiplet. At −25°C, however, each Rh/Me signal is very broad ($\Delta\nu_{1/2}$ = 68 Hz). The $^{31}P\{^1H\}$ NMR spectrum of $RhClMe_2(PMePh_2)_3$ shows two resonances (intensity, 2:1) at 25°C, the less intense one is a broad singlet (i.e. neither P—Rh nor P—P′ coupling is resolved) and the more intense one is a broad doublet ($J_{Rh—P}$ = 110 Hz). This behaviour we attribute to selective dissociation of P_A in eq. (2), due both to the steric bulk of diphenylmethyl phosphine and its location opposite the strong *trans*-directing methyl ligand. The importance of the *trans*-methyl group rests on the observation that *mer*-$RhCl_3(PMePh_2)_3$ shows no line broadening in the $^{31}P\{^1H\}$ NMR; a sharp AM_2X pattern is observed.



$$\rightleftharpoons \quad RhClMe_2(P_B)_2 + P_A \qquad (2)$$

$RhMe_2Cl(PMePh_2)_3$ reveals its crowded character in yet another way (Fig. 1). The P_A—Rh and P_A—P_B coupling which is absent in the P_A resonance at and above 25°C is restored at −10°C; a sharp doublet ($J(P_A—Rh)$ = 76 Hz) of triplets ($J(P_A—P_B)$ = 21 Hz) is observed. However, at

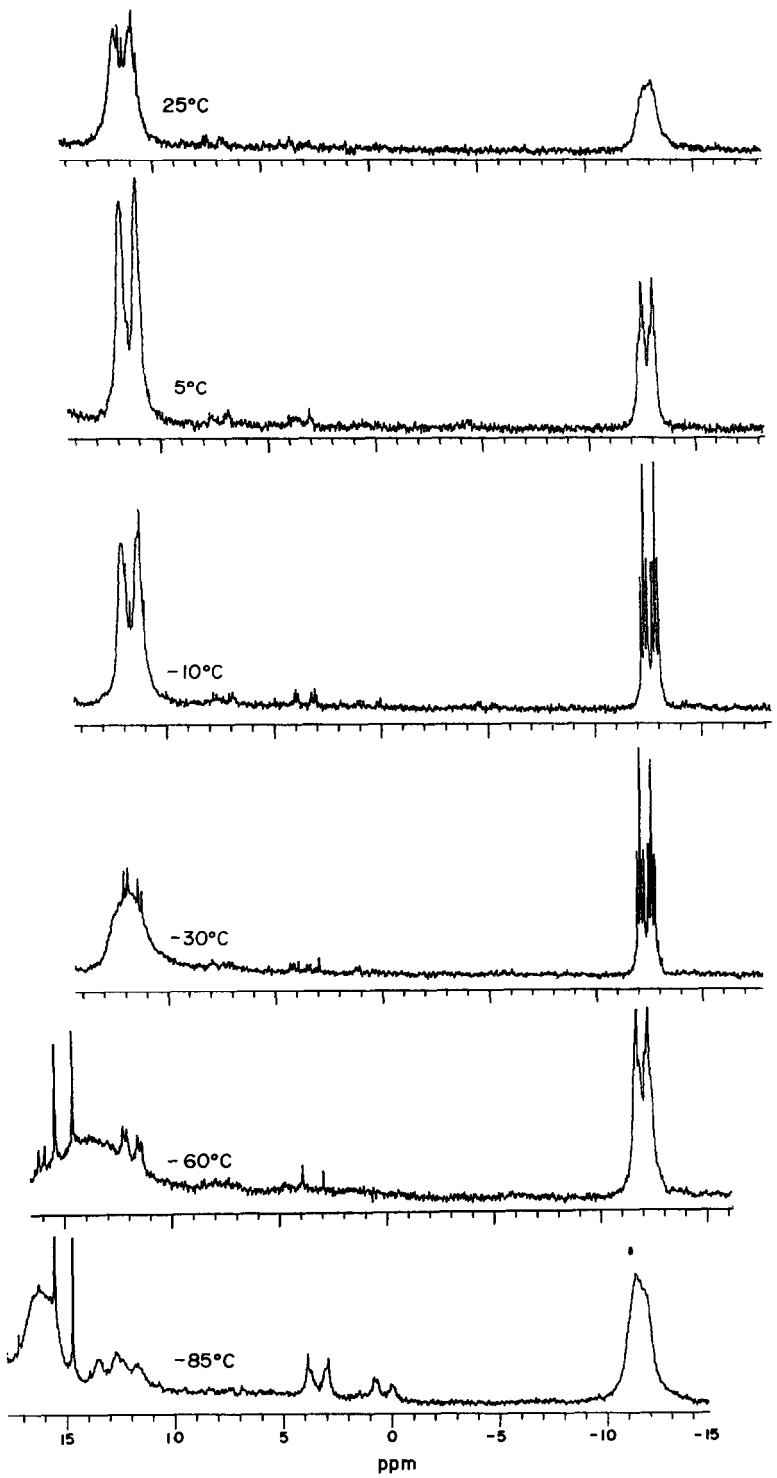


Fig. 1. Variable temperature $^{31}P\{^1H\}$ NMR spectra of $RhMe_2Cl(PMe_2Ph_2)_3$ in CD_2Cl_2. The consistently sharp peaks between 10 and 15 ppm are impurities.

$-10°C$, the P_B resonance is still a doublet of broad lines. At -25 and $-40°C$, the $^{31}P\{^1H\}$ NMR resonance of P_A remains a sharp doublet of triplets, but the P_B doublet becomes increasingly broad. Nevertheless, the sharp P_A—P_B coupling in the P_A resonances assures the lack of significant phosphine dissociation at these temperatures. Finally, at $-85°C$, the P_A resonance is one unresolved broad line and the P_B region now contains several broad lines (no J(P—Rh) observed) indicative of *several* closely spaced chemical shifts undergoing dynamic exchange at an intermediate rate. This we interpret as the freezing out of an ABCX spin system, where B and C are the axial phosphines in $RhMe_2Cl(PMePh_2)_3$, made inequivalent by the freezing out of distinct rotational conformations about the Rh—P and P—C bonds in the T-shaped $Rh(PMePh_2)_3$ substructure. Similar phenomena have been reported by Bushweller for $M(CO)Cl[P(^tBu)_2R]_2$ compounds.[3] Note that no ^{31}P NMR signal of free $PMePh_2$ is seen at (or above) $-85°C$.

DISCUSSION

We feel that the isolation of monohalopolyalkyl compounds during attempted *per*-alkylation of $(R_3P)_mMCl_n$ compounds *under mild conditions* of temperature is a kinetic effect due to the sequential strengthening of the M—Cl bonds (increased Cl→M π-donation) as the number of π-donor ligands decline. Thus, at the stage of $(R_3P)_mMR'_{n-1}Cl$, all π-donation is concentrated in the single remaining M—Cl bond (there being no other π-donor ligands present), and this bond is therefore uniquely resistant to replacement by alkyl. The effect is subtle; there is no evidence of Ir—Cl bond length shortening along the series $IrCl_{3-n}H_n(PMe_2Ph)_3$,[4] so it has only kinetic (not ground state) manifestations, but it may well occur in the unsaturated $RhMe_2ClP_2$ intermediate. Increasing alkylation also would be expected to increase steric suppression of the rate of alkylation.

Based on the above reasoning, we anticipate that this phenomenon would be of even greater importance in the alkylation of *unsaturated* metal halides, where ground-state bond shortening is evident (e.g. $TiCl_4$, where d(Ti—Cl) = 2.170 Å[5] and $TiCl_3(CH_3)$, where d(Ti—Cl) = 2.185 Å[6] vs Cp_2TiCl_2, where d(Ti—Cl) = 2.366 Å,[7] and $Ti(Me_2PC_2H_4PMe_2)Cl_3R$, where d(Ti—Cl) = 2.30–2.32 Å[8]) and thus kinetic effects should be magnified.* This effect should, of course, also be evident whenever π-donor ligands are replaced by purely σ-ligands (e.g. hydrides).

The special tendency of $PMePh_2$ to promote phosphine dissociation in $L_mM(PMePh_2)_n$ complexes ($n \geqslant 3$) is worthy of note, particularly in comparison to the (perhaps) more frequently used PMe_2Ph. The benefits of using this bulky phosphine to furnish 16-electron species are evident in, for example, the C/O multiple bond splitting reactions of Mayer and co-workers[9,10] using $WCl_2(PMePh_2)_4$ (but not the PMe_3 analogue). The close relationship between $PMePh_2$ and PPh_3 is also evident in that $RhMeI_2(PPh_3)_2$, analogous to the transient $RhMe_2Cl(PMePh_2)_2$ implicated above, is an isolable compound.[11]

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* In this regard, note the successful synthesis of $(dmpe)TiCl_3R$ (R = Me, Et).[8]