C-Alkylation of Carbanions Derived from [(MX$_2$(Ph$_2$PCH$_2$PPh$_2$)] (M = Pt or Pd; X = halogen)

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Introduction

We have shown that $Ph_2PCH_2PPh_2$(dppm) – substituted Group VI metal carbonyls, [M(CO)$_4$(dppm)], are deprotonated by strong bases such as MeLi or Bu^{n}Li and the resultant carbanions, $[M(CO)_4(Ph_2PCHPPh_2)]^-$, are readily alkylated or acylated to give derivatives, [M(CO)$_4$(Ph$_2$PCHRPPh$_2$)] (R = alkyl or aryl) [1]. In contrast, the free anion derived from dppm *viz* $[Ph_2PCHPPh_2]^-$ is ambident and can be attacked at carbon and/or phosphorus by electrophiles [2]. We now wish to report that dppm coordinated to platinum(II) or palladium(II) can be similarly alkylated. There is currently much interest in the chemistry of dppm coordinated to platinum or palladium.

Results and Discussion

Clearly, LiMe or LiBu^n might not be satisfactory bases for deprotonation of dppm coordinated to platinum(II) since they are also powerful nucleophiles towards platinum(II) {or palladium(II)}. Thus we have used a very strong but non-nucleophilic (*i.e.* bulky) base, LiN(SiMe$_3$)$_2$. Treatment of a suspension of [PtI$_2$(dppm)] with an equivalent amount of LiN(SiMe$_3$)$_2$ in tetrahydrofuran (THF) for 1½ hour at 20 °C gave a clear yellow solution which, when treated with methyl iodide and heated 45–50 °C for 5 hours, gave [PtI$_2$(Ph$_2$PCHMePPh$_2$)], as yellow prisms from dichloromethane, in 72% isolated yield. The product was characterized by elemental analysis, molecular weight, mass spectrum, and ^{1}H, ^{1}H-{^{31}P} and ^{31}P-{^{1}H} NMR spectroscopy. [PtI$_2$(Ph$_2$PCHEtPPh$_2$)] was similarly prepared in 86% isolated yield and [PtBr$_2${Ph$_2$PCH(CH$_2$Ph)PPh$_2$}] was prepared in 85% yield from [PtBr$_2$(Ph$_2$PCH$_2$PPh$_2$)]. It is noteworthy that uncomplexed $[Ph_2PCHPPh_2]^-$ is attacked by benzyl chloride predominantly at phosphorus [3]. Treatment of [PtI$_2$(Ph$_2$PCH$_2$PPh$_2$)]. with LiN(SiMe$_3$)$_2$/MeI as above followed {without isolation of [PtI$_2$(Ph$_2$PCHMePPh$_2$)]} by a second addition of LiN(SiMe$_3$)$_2$ and then, after a further hour, MeI, gives the dimethylated derivative [PtI$_2$(Ph$_2$PCMe$_2$PPh$_2$)] in 73% overall yield. These new complexes were fully characterized in a similar manner to [PtI$_2$(Ph$_2$PCHMePPh$_2$)] (above).

It seemed possible that the product formed by treating [PtI$_2$(Ph$_2$PCH$_2$PPh$_2$)] with LiN(SiMe$_3$)$_2$ was a carbanion $[PtI_2(Ph_2PCHPPh_2)]^-$, a lithio derivative [PtI$_2$(Ph$_2$PCHLiPPh$_2$)] (more covalent than the carbanion), or a di-iodo bridged complex, [Pt$_2$(μ-I)$_2$(Ph$_2$PCHPPh$_2$)$_2$]. We have attempted to learn something about the nature of the intermediate by means of a ^{31}P-{^{1}H} NMR study. Treatment of [PtI$_2$(dppm)] with LiN(SiMe$_3$)$_2$ (1.05 mole equivalents) in THF gives a single species characterized by a singlet with singlet satellites due to coupling to platinum-195; $\delta(P) = -63.2$ ppm, $^1J(Pt–P) = 2747$ Hz {using deuterioacetone as external reference}. [PtI$_2$(dppm)] in THF shows $\delta(P) = -71.1$ ppm, $^1J(Pt–P) = 2849$ Hz {shifts relative to 85% H$_3$PO$_4$}. The spectrum was also measured at –64 °C and showed no change there being no evidence of a binuclear species *i.e.* no evidence of three bond coupling to platinum-195 nor evidence of coupling to lithium-7. Halo-bridged platinum(II)–PR$_3$ complexes show three bond coupling, $^3J(Pt–P)$ and two bond coupling, $^2J(Pt–Pt)$ [4, 5] and free Ph$_2$PCHLiPPh$_2$ at –73 °C shows well resolved coupling, $^2J(^{31}P–^7Li)$ [6]. Thus we suggest that our intermediate is the free anion $[PtI_2(Ph_2PCHPPh_2)]^-$. We have also done a preliminary study on the methylation of the corresponding palladium complex [PdI$_2$(Ph$_2$PCH$_2$PPh$_2$)]. Treatment of this complex with LiN(SiMe$_3$)$_2$ (1.1 equivalent) followed by methyl iodide (1.1 equivalent) gave a mixture which was mainly [PdI$_2$(Ph$_2$PCHMePPh$_2$)] but it also contained some of the starting complex and the dimethylated complex [PdI$_2$(Ph$_2$PCMe$_2$PPh$_2$)]. This mixture was not separated but its components were characterized by ^{1}H, ^{1}H-{^{31}P} and ^{31}P-{^{1}H} NMR spectroscopy.

We are investigating the possibility of deprotonation/alkylation of binuclear complexes containing (μ-dppm) moieties such as 'A-frames' metal–metal bonded species *etc.* [7, 8].

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