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Preliminary communication

THE FACILE CYCLOMETALLATION REACTION OF 1,3-BIS[(DIPHENYLPHOSPHINO)METHYL]BENZENE

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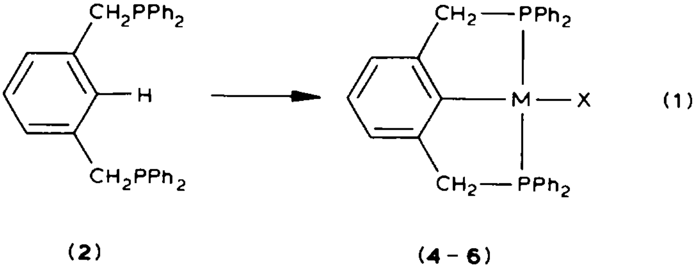
Summary

It is shown that 1,3-bis(diphenylphosphinomethyl)benzene (PCHP) readily undergoes a cyclometallation reaction with nickel(II), palladium(II), and platinum(II) species giving products of the type [MX(PCP)] [M = Ni, Pd, and Pt; X = halide and PCP = 2,6-bis(diphenylphosphinomethyl)phenyl]. Cyclometallation requires the formation of intermediates *trans*-[MX_2(PCHP)].

The chelating diphosphine 1,3-bis(di-t-butylphosphinomethyl)benzene reacts with nickel(II), palladium(II) and platinum(II) compounds giving cyclometallated species such as [MCl(1)], 1 = 2,6-bis(di-t-butylphosphinomethyl)phenyl, and the relative ease of this reaction has been attributed to the effect of the bulky substituents [1].

We report here the reactions of the analogous ligand 1,3-bis(diphenylphosphinomethyl)benzene (2) [2]. This forms cyclometallated derivatives, containing the tridentate moiety 2,6-bis(diphenylphosphinomethyl)phenyl (3) with great ease if the appropriate substrates and reaction conditions are used.



(1)

The reactions carried out and the products obtained are shown in eq. 1 (**4**: M = Pd, X = Cl; from **2** and $[PdCl_2(CH_3CN)_2]$ in CH_2Cl_2, 10 min, room temperature, followed by moist EtOH; 75%. **5a** (**5b**): M = Pt, X = Cl(Br); $\{PtCl_2\}_n$ ($\{PtBr_2\}_n$) in aq. acetone, 10 days, room temperature, ca. 30%. **5c**: M = Pt, X = I; from $[Pt(3)PPh_3]Cl$ (prepared in situ by reacting *cis*-$[PtCl_2(PPh_3)_2]$ and **2** in acetone, 24 h, room temperature) and NaI (excess) in acetone, ca. 65%. **6**: M = Ni, X = Cl, from $NiCl_2 \cdot 6H_2O$ and **2** in EtOH, 3 h 60°C, followed by $(i\text{-}Pr)_2NEt$, 10 min reflux, 69%. All the complexes mentioned above gave satisfactory microanalyses [3]).

It is noteworthy that platinum(II) chloride or bromide (one equivalent in aqueous acetone) react with phosphine **2** giving **5a** or **5b** in moderate yields and mixtures of oligomeric complexes of the type *cis*-$[PtCl_2(3)]_n$ or *cis*-$[PtBr_2(3)]_n$, respectively. However, the reaction of **2** with *cis*-$[PtCl_2(PPh_3)_2]$ in CH_2Cl_2/acetone gives $[Pt(3)PPh_3]^+$ [4] in high yield. The latter, on addition of sodium iodide, gives **5c**.

Compounds **5a** and **5b** react with $NaBH_4$ in moist acetonitrile giving the mononuclear hydride $[PtH(3)]$. However, the corresponding reaction with the palladium complex **4** or the nickel compound **6** lead either to decomposition or to a mixture of unidentified products, respectively.

Our work indicates that the facile cyclometallation of phosphine **2** is mainly due to the geometry of the complex or complexes formed before cyclometallation occurs. Thus compounds of the type *cis*-$[MX_2(2)]$ do not cyclometallate while the corresponding *trans* species, which place the C—H bond which is to be activated close to the metal center, readily react. This is a well-established effect [5]. Thus, it appears likely that the t-butyl substituents on ligand **1** facilitate its cyclometallation reaction by favouring the formation of *trans*-$[PtCl_2(1)]$.

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References

1 C.J. Moulton, B.L. Shaw, J. Chem. Soc. Dalton Trans., (1976) 1020.

2 Prepared by treating 1,3-bis(bromomethyl)benzene with Ph_2PNa in liquid ammonia.

3 Their ^1H and ^{31}P NMR data measured in $CDCl_3$, ($\delta(H) = \delta(^1H)$ (ppm) for CH_2; $J = |^2J(^{31}P, ^1H) + ^4J(^{31}P, ^1H)|$ (Hz); $J' = ^3J(^{195}Pt, ^1H)$ (Hz); $\delta(P) = \delta(^{31}P)$ (ppm) relative to external H_3PO_4; a positive sign indicates a signal downfield of the resonance (ppm); $J'' = ^1J(^{195}Pt, ^{31}P)$ (Hz); s = singlet; t = triplet or pseudo-triplet) are: **2**, $\delta(H)$ 3.88(s), $\delta(P)$ −10.1; **4**, $\delta(H)$ 3.98(t), J 4.7, $\delta(P)$ 33.4; **5a**, $\delta(H)$ 3.90(t), J 4.7, J' 25, $\delta(P)$ 33.1, J 2968; **5b**, $\delta(H)$ 3.89(t), J 4.5, J' 25, $\delta(P)$ 34.2, J'' 2933, **5c**, $\delta(H)$ 3.94(t), J 4.8, J' 25, $\delta(P)$ 35.2, J'' 2884; **6**, $\delta(H)$ 3.85(t), J 4.7, $\delta(P)$ 34.6.

4 NMR data (measured in $CDCl_3$): $^{31}P\{^1H\}$ NMR: $\delta(^{31}P$ of **3**) 41.3(d) ppm; $^1J(^{195}Pt, ^{31}P)$ 2762 Hz; $^2J(^{31}P, ^{31}P)$ 20.6 Hz; $\delta(^{31}P$ of $PPh_3)$ 17.8(t) ppm; $^1J(^{195}Pt, ^{31}P)$ 2008 Hz. ^1H NMR: $\delta(^1H$ of $CH_2)$ 4.42 ppm (pseudotriplet, virtual coupling); $^3J(^{195}Pt, ^1H)$ 31.8 Hz; $|^2J(^{31}P, ^1H) + ^4J(^{31}P, ^1H)|$ 4.3 Hz.

5 M.I. Bruce, Angew. Chem., 89 (1977) 75.