Inorganica Chimica Acta, 30 (1978) L325–L326

Complexes of 1,3-Bis(Dimethylphosphinomethyl)-benzene with Nickel(II), Palladium(II) and Iron(II) Halides

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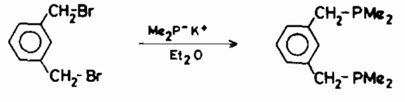
Received June 27, 1978

Introduction

The widely known result of aromatic and benzylic metalation of phosphorus ligands by transition metal atoms has attracted considerable interest [1–5]. There are few known examples of internal aromatic ring matalation by iron(II) although Ikariya and Yamamoto [6] have synthesized the *o*-metalated methyl iron complex $[\mathrm{Fe(CH_3)(Ph_2P{-}CH_2{-}CH_2PPhC_6H_4)}]$ from the dimethyliron complex $[\mathrm{Fe(CH_3)_2(Ph_2PCH_2\text{-}CH_2PPh_2)_2}]$.

We report here the interaction of the benzylic phosphine 1,3-bis(dimethylphosphineomethyl)benzene (dmpx) **1** with iron(II), nickel(II) and palladium(II) halides.

The ligand dmpx is prepared as a colorless oil from the interaction of potassium dimethylphosphine with α,α′-dibromo-*m*-xylene,



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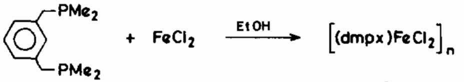
Results and Discussion

Addition of **1** to a solution of hydrated ferrous chloride in degassed ethanol gives a white polymeric precipitate which is insoluble in most organic solvents. Analytic results are consistent with the formulation $[\mathrm{(dmpx)FeCl_2}]_n$ **2**, and the infrared spectrum shows a band at 347 $\mathrm{cm^{-1}}$ which is assigned to ν(Fe–P) and a band at 280 $\mathrm{cm^{-1}}$ for ν(Fe–Cl).

The complex **2** readily dissolves in benzene in the presence of trimethylphosphine or 1,2-bis(dimethylphosphino)ethane (dmpe). These solutions are extremely air sensitive and turn red or light pink with the slightest trace of oxygen. The volatile trimethylphosphine can be easily removed from solutions of $[\mathrm{(dmpx)(Me_3P)_2FeCl_2}]$ by vacuum with the resultant formation of white suspensions of **2**.

The reduction of $[\mathrm{(dmpx)(dmpe)FeCl_2}]$ **3** with a 30% sodium amalgam at 0 °C in THF gives a red-brown pentane soluble product. The infrared spectrum of the product in nujol shows no ν(Fe–Cl) band but does show a band at 1770 $\mathrm{cm^{-1}}$, which is tentatively assigned to ν(Fe–H). The $^1\mathrm{H}\{^{31}\mathrm{P}\}$ NMR spectrum in THF-d_8 shows a resonance at δ1.27 assigned to the methyl protons of dmpx, and a resonance at δ0.90 assigned to the methyl protons of dmpe. The methylene protons occur at δ2.63 and δ2.25 for dmpx and dmpe respectively. Both peaks are broad because of trace paramagnetic impurities.

These data indicate the formation of the metalated *cis* hydrido iron complex, **4**.



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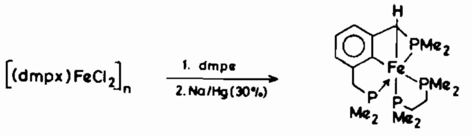

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The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum shows three multiplet resonances at δ53.32, δ30.80, and δ21.77 relative to $\mathrm{H_{13}PO_4}$, which is similar to that observed by Ittel [7].

Evidently reduction of **3** which is formed by addition of dmpe to **2** gives a tetracoordinate Fe(0) complex with *ortho*-metalates the aromatic C–H bond to give the complex **4** [8].

Experimental

Reactions were performed under dry, oxygen free nitrogen or argon in Schlenk-type glassware. Nonhydroxylic solvents were distilled from sodium benzophenone ketyl under argon. Hydroxylic solvents were dried over 3Å molecular sieves and degassed by purging with nitrogen or using the freeze–thaw technique.

NMR spectra were obtained with Varian T-60 or XL-100 instruments (Nicolet TT-100, PFT equipment). The $^1\mathrm{H}$ chemical shifts are reported in ppm downfield from TMS and the $^{31}\mathrm{P}$ chemical shifts are reported in ppm downfield from $\mathrm{H_3PO_4}$ as positive.

Infrared spectra were obtained on P.E. 337 and P.E. 283 grating spectrophotometers. Elemental analyses were performed by Chemanalytics, 2330 S. Industrial Park Drive, Tempe, Arizona 85281.

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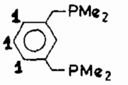
TABLE I. ^1H NMR and ^{31}P NMR Data for Dmpx.

	$^1H^a$				$^{31}P^a$		
	δMe	δCH_2	δH_1	δH_2	$\delta ^{31}P$	J_{P-Me}	J_{P-CH_2}
	0.80(d)	2.53	6.93	7.15	46.5	3 Hz	3 Hz

^{a}In benzene.

Synthesis of 1,3-Bis(dimethylphosphinomethyl)benzene, 1

Dimethylphosphine (3.5 g; 0.06 mol) in 5 ml of dry THF is added to a slurry of KH (2.49 g; 0.06 mol) in 40 ml of THF at –78 °C. Overnight stirring at –78 °C gives a yellow-brown suspension of potassium dimethylphosphide, to which is added α,α'-dibromomethyl-*m*-xylene (7.9 g; 0.03 mol) in 20 ml of THF at –78 °C. After allowing the mixture to reach room temperature, the solution is filtered from KCl and excess THF removed to give a crude oil, which is purified by vacuum distillation, 4 g (30%; 140 °C/1 mm).

Direct quaternization of α,α'-dibromo-*m*-xylene with dimethylphosphine and subsequent treatment with base gave only trace amounts of the desired product and much insoluble material.

The ligand dmpx is a colorless air sensitive oil which is characterized by its mass spectrum as the bis(phosphine oxide). *Anal.* Calcd. for *m*-$[(CH_3)_3P(O)CH_2]_2C_6H_4$, m/e 258.095. Found: m/e 258.094.

The Synthesis of $[(dmpx)FeCl_2]_n$, 2

Hydrated ferrous chloride (0.439 g; 2.21 mmol) in ethanol is added to a solution of dmpx (0.50 g; 2.21 mmol) in ethanol. The mixture is stirred for 1 hr and the white precipitate is separated by filtration and dried under vacuum (0.46 g; 59%). The material can also be obtained by refluxing excess dmpx with a slurry of anhydrous ferrous chloride in benzene for one and one-half hours (0.51; 65%). *Anal.* Calcd. for $C_{12}H_{20}P_2FeCl_2$: C, 40.83; H, 5.71; Cl, 20.09. Found: C, 40.10; H, 5.30; Cl, 20.33.

(dmpx)(dmpe)FeCl₂ and Na(Hg), 4

Dmpe (0.09 g; 0.60 mmol) is added to a suspension of $dmpxFeCl_2$ in 10 ml of THF. The white solid slowly dissolves to give a slightly pink solution. This pink solution is added to sodium amalgam (0.27 g; 2.98 mmol; 30% amalgam) in THF at 0 °C, and stirred for 8 hours. The mixture is filtered at room temperature and THF removed to give a red-brown residue which is extracted with pentane and filtered again. Removal of pentane gives a red-brown solid. The solid proved to be too exceedingly air sensitive for commercial analyses.

1,3-Bis(dimethylphosphinomethyl)benzene Nickel(II) Chloride

A solution of dmpx (0.145 g; 0.64 mmol) in deoxygenated ethanol is treated with a solution of nickel chloride hydrate (0.153 g; 0.64 mmol) in ethanol. The precipitated pale red crystals are collected by filtration, washed with ethanol and dried under vacuum (0.13 g; 60%). *Anal.* calcd. for $C_{12}H_{20}P_2NiCl_2$: C, 40.50; H, 5.67; Cl, 19.92. Found: C, 42.75; H, 5.79; Cl, 19.49.

1,3-bis(dimethylphosphinomethyl)benzene Palladium(II) Chloride

A solution of bis(benzonitrile)palladium chloride (0.560 g; 1.46 mmol) in 10 ml of methoxy ethanol is treated with DMPB (0.38 g; 1.47 mmol) in methoxy ethanol. The mixture is briefly heated, then cooled to room temperature and the yellow product precipitated with ethanol. After filtration and drying under vacuum (0.25 g; 49%) of yellow solid is isolated. *Anal.* Calcd. for $C_{12}H_{20}P_2Cl_2Pd$: C, 35.72; H, 5.00; Cl, 17.57. Found: C, 31.83; H, 4.60; Cl, 16.36.

Acknowledgement

We are grateful to the Petroleum Research Fund Administered by the American Chemical Society for partial support of this research, J. C. Baldwin for the ^1H and ^{31}P NMR spectra, and J. Bupp for the mass spectra.

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8 The complex $\{(dmpx)(Me_3P)_2\}FeCl_2$ is also readily reduced with Na(Hg) in THF. The ^1H NMR spectrum in C_6D_6 shows a doublet of doublets for inequivalent protons on the Me_3P groups, δ1.0 and δ0.6. The dmpx ligand shows resonances at δ1.2 $(CH_3)_2P$, multiplet; CH_2–P, δ2.4 multiplet and C_6H_3, δ7.0, singlet. The $^{31}P\{^1H\}$ NMR spectrum shows three multiplet resonances at δ53.8, δ44.8 and δ38.3.