

The cyclometallation of bis(di-*p*-methylbenzylphosphino)methane

Alberto Fernández ¹, José M. Vila *

Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

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Abstract

The new diphosphine (4-MeC₆H₄CH₂)₂PCH₂P(4-MeC₆H₄CH₂)₂, **L**, was reacted with [MnMe(CO)₅] to give the novel cyclometallated compound [Mn{(4-MeC₆H₃CH₂)(4-MeC₆H₄CH₂)PCH₂P(4-MeC₆H₄CH₂)₂}(CO)₃], as the *mer* isomer, and with the ligand in a terdentate [C,P,P] fashion.

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1. Introduction

Transition metal cyclometallated compounds comprise a rich and fruitful research field within organometallic chemistry [1–7], due in part to the numerous available metals [8], but mainly to the ever growing versatility of the organic ligands [8], which renders a nearly limitless range of substrates that may be employed in the metallation reaction; nitrogen-donor species, on the one hand, and palladium and platinum, on the other, are the more frequently used ligands and metals, respectively. Cyclometallation may also be achieved through phosphorus-donor ligands, which likewise give rise to a great range of compounds [9] and it has been shown that tertiary phosphines with bulky groups on the phosphorus atom [10a] as well as formation of five-membered metalacycles [8] is paramount to the cyclometallation process, although tertiary phosphines can also form compounds with four-membered rings [10]. Herein, we report the cyclometallation of the short chain diphosphine bis(di-*p*-methylbenzylphosphino)methane.

2. Results and discussion

Addition of bis(dichlorophosphino)methane to an ethereal solution of *p*-methylbenzylmagnesium bromide gave the new diphosphine (4-MeC₆H₄CH₂)₂PCH₂P(4-MeC₆H₄CH₂)₂, **L**, as a white solid which was fully characterised (see Section 3). The AA'XX' pattern of the four phenyl ring protons appear as a broad signal which integrates for 16 H; four singlets at δ2.36, δ2.34, δ2.33 and δ2.31 were assigned to the *p*-Me groups.

Treatment of **L** with [MnMe(CO)₅] in *n*-octane gave the unprecedented cyclometallated manganese (I) compound [Mn{(4-MeC₆H₃CH₂)(4-MeC₆H₄CH₂)PCH₂P(4-MeC₆H₄CH₂)₂}(CO)₃], **1**, as a yellow solid, with the diphosphine as terdentate [C, P,P], which was fully characterised (see Section 3). The reaction was monitored by close inspection of the carbonyl region in the infrared spectrum. The final product consisted of only one of the two possible isomers, i.e., the *mer* moiety, as opposed to the metallation of PMe₂(CH₂Ph) where both isomers were obtained [11]. Thus, the IR spectrum showed three ν(CO) bands characteristic of a *mer*-M(CO)₃ group at 1980s, 1905s, 1880s cm⁻¹. The ¹H NMR spectrum showed the resonances due to the metallated ring protons: H3, H5 and H6, at δ6.91s, δ6.79d and δ6.35dd, respectively, the latter coupled to the ³¹P

* Corresponding author. Tel.: +3481528073; fax: +3481595012.
E-mail address: qideport@usc.es (J.M. Vila).

¹ Present address: Departamento de Química Fundamental, Universidad de La Coruña, 15071 La Coruña, Spain.

nucleus (see Section 3 and Scheme 1); a complex signal, integrating for 12H, was assigned to three sets of AA'XX' protons of the remaining phenyl rings. The $^{31}\text{P}\{-^1\text{H}\}$ spectrum showed two doublets at $\delta 47.22$ (P *trans* to Ph) and $\delta 23.01$ (P *trans* to CO), assigned to the two inequivalent phosphorus atoms. The assignment of the doublets was made on the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [12]. The carbon-13 NMR spectrum was in agreement with the assigned structure. The carbonyl resonances were at $\delta 211.3$ (due to the two mutually *trans* carbons) and at $\delta 197.4$ (*trans* to phosphorus) (see Section 3). The CMn and C1 resonances were at $\delta 149.78$, and $\delta 139.15$, respectively, downfield shifted as compared to the other phenyl carbon signals consequent upon metallation of the phenyl ring, the former appeared coupled to both phosphorus nuclei; the $\text{CH}_2\text{C}_6\text{H}_3$ carbon resonance was also slightly downfield shifted, and coupled to only one phosphorus nuclei.

As opposed to monodentate *o*-tolylphosphines, which are readily metallated at the methyl group [13], chelating phosphines $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ($n = 2, 3$) are very resistant to internal metallation by palladium or platinum, and only for $n = 3$, has this been reported [14]; for $n = 1$, metallation would seem even more difficult due to the rigidity of the chelate ring, which restricts the approach of the *ortho*-carbon atom of the phenyl ring group towards the metal. However, the analogous diphosphine, bis(*di-p*-methylbenzylphosphino)methane, **L**, having greater flexibility induced by the methylene group on the phosphorus atom, should enable the aromatic ring to approach the metal center, and to enhance the easiness with which metallation is produced. As for electronic effects it is known that substitution of a methyl group in the *para* position on a tertiary arylphosphine increases the tendency of the ligand to under-

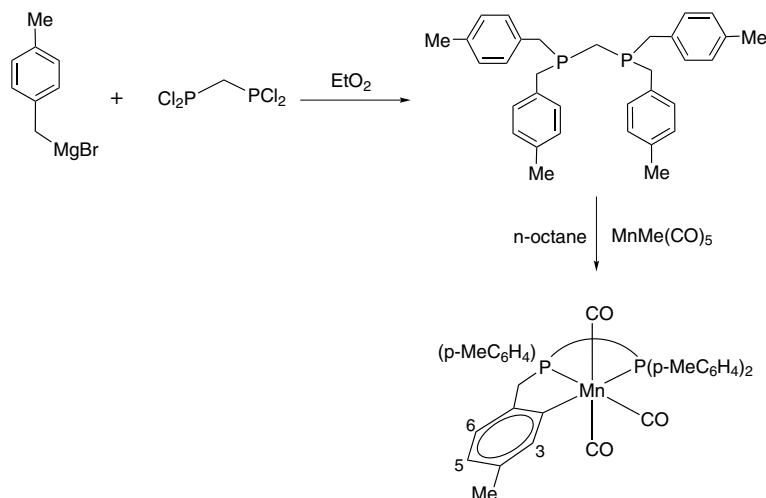
go *ortho*-metallation with platinum (II) complexes [10a] and that electron-withdrawing substituents activate the ring to attack by nucleophilic reagents, whilst electron-donating substituents activate the ring towards electrophilic attack [15]. However, in the present case the *p*-Me substituted ring could only be metallated by Mn(I); attempts with Pd(II) and Pt(II) failed. Furthermore, methyl groups on metals such as rhodium or platinum promote internal metallation of tertiary phosphine ligands [16]; disappointingly, we have found this not to be the case for $[\text{PtMe}_2(\text{COD})]$ which failed to metallate the title ligand, **L**; however, with $[\text{MnMe}(\text{CO})_5]$ the diphosphine ligand was readily metallated.

3. Experimental

All reactions were carried out in an atmosphere of dry nitrogen. Solvents were purified by standard methods [17]. Chemicals were reagent grade. $[\text{MnMe}(\text{CO})_5]$ was prepared as reported [18]. The phosphine $\text{Cl}_2\text{PCH}_2\text{PCH}_2\text{Cl}_2$ was purchased from Strem chemicals. Microanalyses were carried out using a Carlo-Erba Elemental Analyser, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as CDCl_3 or $(\text{CD}_3)_2\text{SO}$ solutions and referenced to SiMe_4 (^1H , ^{13}C) or 85% H_3PO_4 ($^{31}\text{P}\{-^1\text{H}\}$) and were recorded with Bruker AMX 300, AMX 500 and WM250 spectrometers. All chemical shifts were reported downfield from standards.

3.1. Synthesis of $(4\text{-MeC}_6\text{H}_4\text{CH}_2)_2\text{PCH}_2\text{P}(4\text{-MeC}_6\text{H}_4\text{CH}_2)_2$

Magnesium turnings (1.110 g, 45.58 mmol) and a catalytic amount of iodine were added in anhydrous ethyl



Scheme 1.

ether (40 cm³). Then, α -bromo-*p*-xylene (8.470 g, 45.78 mmol) in diethyl ether (40 cm³) was added dropwise and the resulting mixture was refluxed for 1.5 h. To the cooled reaction bis(dichlorophosphino)methane (1.458 g, 6.70 mmol) in diethyl ether (40 cm³) was added dropwise and stirred for 12 h. Ammonium chloride in water (9 g/100 cm³) was added, stirring continued for a further 30 min, the mixture extracted with four 50 cm³ portions of ethanol and the combined extracts reduced to low volume under vacuum. The residue was recrystallized from methanol to give a white solid, which was filtered off and dried in vacuo. Yield: 70%. C₃₃H₃₈P₂ (496.61). Anal. Found: C, 79.9; H, 7.6%. Calc.: C, 79.8; H, 7.7. ¹H NMR: δ 7.1 (m, 16H, C₆H₄) δ 3.0 (m, 10H, PCH₂P, PCH₂Ph), δ 2.36 (s, 3H, Me), δ 2.34 (s, 3H, Me), δ 2.33 (s, 3H, Me), δ 2.31 (s, 3H, Me). ³¹P-¹H NMR: δ 23.32s.

3.2. Synthesis of [Mn{(4-MeC₆H₃CH₂)-(4-MeC₆H₄CH₂)PCH₂P(4-MeC₆H₄CH₂)₂}(CO)₃]

The diphosphine (4-MeC₆H₄CH₂)₂PCH₂P(4-MeC₆H₄CH₂)₂ (100 mg, 0.200 mmol) and [MnMe(CO)₅] (42 mg, 0.200 mmol) were added to *n*-octane (50 cm³). The mixture was heated under reflux (after 15 min a yellow color appears) for 7 h. After cooling to room temperature, the solvent was removed under vacuum and the residue chromatographed in a column packed with silica gel. Elution with dichloromethane gave a yellow band from which the final product was obtained as a yellow solid. Yield: 50%. C₃₆H₃₇O₃P₂Mn (634.57). Anal. Found: C, 68.0; H, 5.8%. Calc.: C, 68.1; H, 5.9. IR: ν (C=O) 1980s, 1905s, 1880s cm⁻¹. ¹H NMR: δ 6.91 (s, 1H, H3), δ 6.79 (d, 1H, H5, ³J(H5H6) = 6.8 Hz), δ 6.35 (dd, 1H, H6, ⁴J(PH6) = 6.1 Hz), δ 3.1 (m, 4H, PCH₂P, PCH₂Ph), δ 2.37 (s, 3H, Me), δ 2.34 (s, 3H, Me), δ 2.27 (s, 3H, Me), δ 2.24 (s, 3H, Me).

¹³C-¹H NMR: δ 197.4 (dd, CO, ²J(PC) = 15.6, 9.5 Hz); δ 211.3 (t, 2CO, ²J(PC) = 8.2 Hz); 149.78 (dd, C Mn, ²J(PC) = 17, ³J(PC) = 5.3 Hz); 139.15 (d, C1, ²J(PC) = 17 Hz); 135.43 (d, C6, ³J(PC) = 4.2 Hz); 134.5–132.7 (m, several CH); 132.4 (CH); 132.2 (d, CH, ³J(PC) = 3.1 Hz); 132.1 (CH); 132.0, 131.9, 131.7, 131.5 (s, 4C_p); 130.2 (s, C3); 129.9 (d, C_i, ²J(PC) = 17.1 Hz); 128.13 (d, C_i, ²J(PC) = 17.0 Hz); 127.85 (d, C_i, ²J(PC) = 17.3 Hz); 126.1 (CH); 125.7

(CH); 125.3 (CH); 124.7 (CH); 39.2 (d, CH₂C₆H₃, ¹J(PC) = 28.0 Hz); 32.6 (d, CH₂, ¹J(PC) = 27.5 Hz); 32.4 (d, CH₂, ¹J(PC) = 27.1 Hz); 32.0 (d, CH₂, ¹J(PC) = 28.2 Hz); 25.1 (d, PCH₂ P, ¹J(PC) = 26.5 Hz); 20.92, 20.85, 20.75, 20.70 (s, 4Me). ³¹P-¹H NMR: δ 47.22d, δ 23.01d (²J(PP) = 83.3 Hz).

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