Journal of Organometallic Chemistry, 73 (1974) C25—C27
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF PHENYLACETYLMANGANESEPENTACARBONYL WITH PHOSPHINE AND PHOSPHITE LIGANDS

M. YORK DARENSBOURG, D.J. DARENSBOURG and D. DREW*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118 (U.S.A.)

(Received March 15th, 1974)

Summary

The reaction of $\mathrm{PhCH_2C({=}O)Mn(CO)_5}$ with 1,2-bis(diphenylphosphino)-ethane has resulted in the formation of $\mathrm{PhCH_2C({=}O)Mn(CO)_3(diphos)}$ which did not undergo decarbonylation. On the other hand $\mathrm{PhCH_2C({=}O)Mn(CO)_5}$ was observed to react with $\mathrm{(PhO)_3P}$ to give initially $\mathrm{PhCH_2Mn(CO)_4P(OPh)_3}$ which further reacted with $\mathrm{(PhO)_3P}$ to eliminate toluene and give the *ortho*-metalated product, $\mathrm{(PhO)_3P\overline{Mn[(PhO)_2P\text{-}\mu\text{-}OC}_6H_4](CO)_3}$.

There is much current interest in aromatic metalation reactions in transition metal complexes containing phosphine and phosphite ligands possessing aromatic rings [1, 2]. In this connection we wish to report observations made in our laboratories of reactions of phenylacetylmanganese pentacarbonyl with phosphine and phosphite ligands.

Kaesz and coworkers [3] have reported the preparation of $\mathrm{Ph_2\overline{P\text{-}\mu\text{-}C_6H_4Mn}(CO)_4}$ from the thermal decomposition of $\mathrm{CH_3Mn(CO)_4PPh_3}$ in refluxing toluene. We have investigated the reaction between $\mathrm{PhCH_2C({=}O)Mn(CO)_5}$ with $\mathrm{Ph_3P}$ in various solvents (THF, toluene, and heptane) with 1/1 or 2/1 mole ratios of $\mathrm{Ph_3P}$ to complex. In all cases initial decarbonylation was observed with the formation of *cis*-$\mathrm{Ph_3PMn(CO)_4CH_2Ph}$ (IR spectral pattern typical of *cis* complexes with ν(CO) 2050 m, 1987 m, 1963 s, 1936 m $\mathrm{cm^{-1}}$; δ ($\mathrm{CH_2}$, protons) 1.74 ppm in $\mathrm{CDCl_3}$ with J(P—H) 5.8 Hz). Further reaction of $\mathrm{Ph_3PMn(CO)_4}$-$\mathrm{CH_2Ph}$ was very slow with appreciable decomposition occurring only after 4—5 days at reflux. New band patterns in the ν(CO) region were complex indicating product mixtures. Although there were some differences in product formation with solvent and mole ratio of $\mathrm{Ph_3P}$, under no conditions was $\mathrm{Ph_2\overline{P\text{-}\mu\text{-}C_6H_4Mn}(CO)_4}$ observed. It is possible that other metallated products similar to those reported by Kaesz and coworkers [4] are present, however,

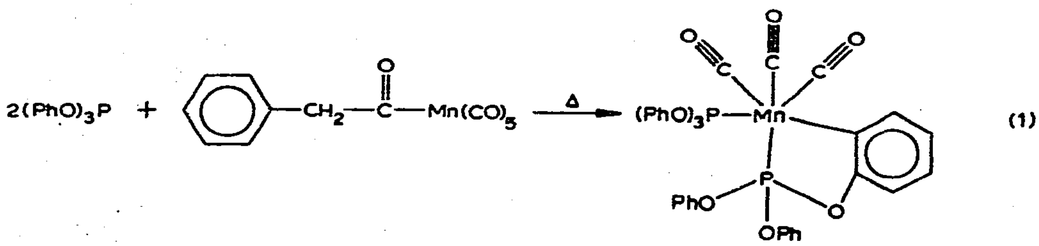
---

*Petroleum Research Fund Postdoctoral Fellow.

separation and isolation of pure compounds have not been effected as yet despite repeated attempts at column chromatography and recrystallization. It should be noted that the product mixture displays a marked air-sensitivity.

Reaction of $PhCH_2C(=O)Mn(CO)_5$ with a 1/1 mole ratio of 1,2-bis(diphenylphosphino)ethane in THF at 55°C for 12 h led to the production of $PhCH_2C(=O)Mn(CO)_3$(diphos), a yellow powder which was recrystallized from benzene—hexane to give a 47% yield of yellow crystals (m.p. 178—179°). (Anal. Found: C, 68.08; H, 4.92; mol. wt., 680. $C_{37}H_{31}P_2O_4Mn$ calcd.: C, 67.69; H, 4.76%, mol. wt., 656.5) The complex was shown to be the *facial* isomer by the presence of two bands in the ν(CO) region in THF at 1992 cm^{-1} (A_1) and 1909 cm^{-1} (E) of intensity ratio 1 to 2. The acyl vibration, ν(C=O), was observed at 1606 cm^{-1}. The NMR spectrum showed a complex multiplet at 7.33 ppm for the phenyl protons, a singlet at 3.87 ppm for the benzyl methylene protons, and a sextet at 3.33 and pentet at 2.59 ppm for the ethylene protons in diphos, in the predicted intensity ratio. Attempts to decarbonylate this product in the solid state at 90° under vacuum for 24 h led to complete recovery of starting material.

In contrast to the above reactions, when $PhCH_2C(=O)Mn(CO)_5$ and $P(OPh)_3$ in a 1/2 mole ratio were heated in hexane at 55° for 20 h,the product $PhCH_2Mn(CO)_4P(OPh)_3$ was observed. Upon further refluxing for 12 h a new species was formed as indicated by the infrared spectrum. Cooling of the solution resulted in formation of a white precipitate which was filtered, washed with hexane and recrystallized from boiling hexane as white needles (yield ~40%, m.p. 129—130°). The analysis was consistent with the formulation of the complex as the aromatic metalated product* (Eqn. 1). (Anal. Found: C, 62.00; H, 4.00; mol. wt., 790. $C_{39}H_{29}O_9P_2Mn$ calcd.: C, 61.75; H, 3.85%; mol. wt., 758.6.) The IR spectrum in the carbonyl stretching region exhibits three bands, 2035.0 s, 1979.0 s, and 1950.3 s cm^{-1} in hexane. Relative intensity measurements of these bands (1/1/1) suggested the assignment of the highest energy band to an A_1 and the two lower bands to the E vibration (split) of the *facial* isomer. Thus the intensity ratio of $1(A_1)/2(E)$ is as expected for the *facial* configuration whereas characteristic spectra of *meridial* isomers show a weak, strong, medium 3-band pattern. A mull infrared spectrum of the complex contained bands at 1100 and 803 cm^{-1} which were not observed in the spectra of the "free" ligand $(PhO)_3P$ or of $(PhO)_3PFe(CO)_4$ and $[(PhO)_3P]_2Fe(CO)_3$. Similar absorptions at 1100 and 800 cm^{-1} have



(1)

---

*This product would presumably result from loss of toluene in the $[(PhO)_3P]_2Mn(CO)_3CH_2Ph$ intermediate. Unlike Kaesz's results [3] where elimination of methane occurred in $[Ph_3P]Mn(CO)_4CH_3$, in our system it was first necessary to add an additional triphenylphosphite ligand prior to the metalation step.

been observed in the infrared spectrum of $[(PhO)_3P]_3Ru(P(OPh)_2OC_6H_4)Cl$ [5, 6] and at 1105, 1038, and 800 cm^{-1} in the iridium complex, $IrHCl[(C_6H_4O)(PhO)_2P][P(OPh)_3]_3$ [7]. These bands are believed to serve as valuable confirmation of the presence of the bidentate ligand, $P(OPh)_2(OC_6H_4)$. The NMR spectra of this complex in both benzene-d_6 and acetone-d_6 show a set of peaks in the region 6.5—8 ppm. The splitting pattern was complicated and no analysis is given here. Loss of the benzyl group was further confirmed by the absence of a peak in the methylene region. The complex did not add molecular hydrogen at atmospheric pressure in THF solution, nor did it react with HCl either in THF solution or in the solid state[*].

The reaction of $(PhO)_3P$ and $PhCH_2C(=O)Mn(CO)_5$ to yield the metalated product was successfully carried out in refluxing THF, heptane, and toluene as well.

Acknowledgment

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the Research Corporation for a grant for the purchase of the Perkin—Elmer 521 infrared spectrophotometer used in this study.

References

1 G.W. Parshall, Accounts Chem. Res., 3 (1970) 139.
2 H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 242, section II.C.4.
3 R. Hoxmeier, B. Deubzer and H.D. Kaesz, J. Amer. Chem. Soc., 93 (1971) 536.
4 R.J. McKinney, B.T. Huie, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 95 (1973) 633.
5 G.W. Parshall, W.H. Knoth, and R.A. Schunn, J. Amer. Chem. Soc., 91 (1969) 4990.
6 J.J. Levison, S.D. Robinson, J. Chem. Soc., A, (1970) 639.
7 M.A. Bennett and R. Charles, Chem. Commun., (1970) 427.
8 B.L. Booth and R.N. Haszeldine, J. Chem. Soc., A, (1966) 157.

---

[*] Booth and Haszeldine [8] have prepared the expected product of H_2 addition to our complex, *cis*- or *trans*-$HMn(CO)_3[P(OPh)_3]_2$. In addition, these workers report that the *cis* isomer eliminates H_2 at 50—60° in toluene to give an unidentified product. However, their product has different physical and spectral properties from our complex and from its molecular weight it appears to be a dimeric structure, possibly $[\overline{Mn_2(CO)_6[P(OPh)_2\text{-}\mu\text{-}OC}_6H_4]_2[P(OPh)_3]_2$.