Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

STRUCTURES OF ACETYL- AND METHYLMANGANESE CARBONYL COMPLEXES OF CHELATING DIPHOSPHINES

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(Received July 8th, 1969)

A continuation of our earlier studies[1,2] on the mechanism of formation of substituted acetylmanganese carbonyl complexes has included an examination of the reactions of chelating diphosphines with methylmanganese pentacarbonyl. Again, as has been so important in the earlier work, clues leading to the structures of the products have been sought through the complementary utilization of ^{1}H NMR and IR spectral observations. In this report, we wish to present evidence which indicates that $CH_3COMn(CO)_3$Diphos, where Diphos is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, has a mutual *cis* configuration and not the *trans* configuration reported earlier[3,4].

The new compound $CH_3COMn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ has been synthesized and as is shown in Table 1 has IR bands whose positions and intensities are very similar to those of the previously reported complex with Diphos as the

TABLE 1

IR AND ^{1}H NMR OBSERVATIONS

Compound	IR (cm^{-1})[a]		^{1}H NMR (τ)[b]		
	ν(C≡O)	ν(C=O)	CH_3CO	CH_3Mn	P–$(CH_2)_n$–P
$CH_3COMn(CO)_3$Diphos	1999 s, 1916 s (br)	1588 s	7.66(1)		[c]
$CH_3COMn(CO)_3$–$[(C_6H_5)_2PCH_2P(C_6H_5)_2]$	1999 s, 1919 s (br)	1585 s	7.27(1)		5.40(12)[d]
$CH_3Mn(CO)_3$Diphos	1994 s, 1917 m, 1890 m			10.85(3)[e]	7.77(?)[f]
$CH_3Mn(CO)_3$–$[(C_6H_5)_2PCH_2P(C_6H_5)_2]$	1997 s, 1918 m, 1893 m			9.993(3)[g]	6.73(12)[h]

[a] Dichloromethane solutions; obtained with a Perkin–Elmer 621 Spectrophotometer; s, strong; m, medium; (br), broad. [b] Benzene solution; obtained with a Varian A-60 ^{1}H NMR Spectrometer; internal TMS at $\tau = 10$; multiplicity in parenthesis. [c] Signal position cannot be assigned. [d] Center of AB quartet of triplets: $\Delta_A - \Delta_B = 1.20$ ppm; $J_{AB} = 15.1 \pm 0.1$ Hz; $J_{AP} = 12.3 \pm 0.2$ Hz; $J_{BP} = 9.7 \pm 0.1$ Hz. [e] $J_{HP} = 10.0 \pm 0.1$ Hz. [f] Center of broad unresolvable signal. [g] $J_{HP} = 10.6 \pm 0.3$ Hz. [h] Center of AB quartet of triplets; $\Delta_A - \Delta_B = 0.25$ ppm; $J_{AB} = 15.1 \pm 0.1$ Hz; $J_{AP} = 10.1 \pm 0.3$ Hz; $J_{BP} = 9.5 \pm 0.2$ Hz.

chelating ligand. We take this as prima facie evidence that these two acetyl complexes have identical structures. Unfortunately, no definitive evidence regarding the structure of the Diphos complex is forthcoming from its ^1H NMR spectrum owing to the inability to unequivocally locate the signals arising from the aliphatic protons of Diphos. However, the ^1H NMR spectrum of $CH_3COMn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ is most informative and clearly indicates that the methylene protons of the phosphine ligand are environmentally non-equivalent. More specifically, the nuclear spins of the methylene protons interact to yield an AB quartet and each of the four lines is split into a 1/2/1 triplet by two equivalent phosphorus nuclei. Two slightly different H–P coupling constants are calculated as might be expected for the interaction of the non-equivalent protons with the equivalent phosphorus nuclei. The pertinent results have been summarized in Table 1. The only conclusion consistent with these observations is that the complex with $(C_6H_5)_2PCH_2P(C_6H_5)_2$ must have a mutual *cis* configuration. The occurrence of only two stretching bands due to C≡O groups attached to the metal in the IR spectra of the two acetyl complexes reported here could indicate a *trans* assignment as suggested earlier. However, a closer examination indicates that the half-width of the lower energy band is about three times that of the higher energy band for each complex as would be expected for overlap of two close lying fundamentals.

The spectral results summarized in Table 1 for two new compounds $CH_3Mn(CO)_3(L–L)$, where L–L are the chelating phosphines examined here, provide further support to the structures suggested for the acetyl complexes. To begin, the IR spectrum of each complex contains three medium to strong metallocarbonyl stretching bands as expected for a group of three mutually *cis* carbonyl groups under C_S symmetry. The positions and intensities of the bands are such as to suggest that the acetyl and methyl complexes have identical structures. Also, the sum of the intensities of the two lower energy bands for the methyl complexes are equal to the intensities of the broad lower energy bands noted for the acetyl complexes. Next, the protons of the methyl group in each complex interacts with two equivalent phosphorus atoms to yield a ^1H NMR signal which is a 1/2/1 triplet thus verifying a mutual *cis* configuration. If one phosphorus were *cis* to the methyl group and the other *trans*, two different coupling constants would arise and two doublets would be expected. Most importantly, a twelve line ^1H NMR signal is observed for the methylene protons in $CH_3Mn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ which is consistent with only a mutual *cis* configuration. The analogous Diphos complex must also therefore have a mutual *cis* structure based on the apparent equivalent positioning of the two phosphorous atoms and its IR spectrum. No other supporting information is obtainable from its ^1H NMR spectrum owing to the breadth of the phosphine ligand aliphatic proton signal.

In conclusion, the mutually *cis* structural assignment proposed here for both $CH_3COMn(CO)_3$Diphos and the corresponding $(C_6H_5)_2PCH_2P(C_6H_5)_2$ analog are in agreement with our earlier more general observation that with non-chelating phosphines, the first formed disubstituted $CH_3COMn(CO)_3L_2$ complex has a mutually *cis* structure. Obviously, further rearrangement of the type observed earlier is impossible with the chelating ligands owing to their ability to span only adjacent coordination sites on the metal. We should also mention that the two methyl derivatives reported here appear to be the first examples of bisphosphine substituted complexes with a mutually *cis* structure.

EXPERIMENTAL

General

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were obtained on samples sealed in nitrogen-filled capillary tubes. The numbering scheme and naming is similar to that employed earlier[2].

$CH_3COMn(CO)_3(L\text{–}L)$ complexes

2,3-[1,2-*Bis(diphenylphosphino)ethane*]-1-*acetylmanganese tricarbonyl.* This compound was prepared as reported earlier[3]. However, recrystallization of the compound from a THF/n-hexane mixture yields a solvate which melts at 154–157° and appears to have the stoichiometry complex $\cdot \frac{1}{2}$ THF based on integration of the NMR spectrum of this product. Recrystallization from a dichloromethane/ether mixture yields the pure product, m.p. 162° (lit.[3] 162°).

2,3-[*Bis(diphenylphosphino)methane*]-1-*acetylmanganese tricarbonyl.* A mixture of 0.21 g (1.00 mmol) of $CH_3Mn(CO)_5$ and 0.42 g (1.10 mmol) of bis(diphenylphosphino)methane in 10 ml of THF was allowed to react for 48 h at room temperature under nitrogen. The light yellow solution was filtered under nitrogen and the volume of the filtrate was reduced to approximately 2 ml with a stream of nitrogen. Addition of 10 ml of n-hexane to the concentrated solution caused precipitation of a light yellow solid, which was collected by filtration washed with n-pentane and dried under a stream of nitrogen. Recrystallization from a 1/3 benzene/n-hexane mixture yielded 0.30 g (53%) of pale yellow crystals m.p. 177.0–178.5°. (Found: C, 64.00; H, 4.45. $C_{30}H_{25}MnO_4P_2$ calcd.: C, 63.67; H, 4.21%.)

$CH_3Mn(CO)_4(L\text{–}L)$ complexes.

2,3-[1,2-*Bis(diphenylphosphino)ethane*]-1-*methylmanganese tricarbonyl.* A solution of 0.50 g (0.86 mol) of 2,3-$CH_3COMn(CO)_3[P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]$ in 15 ml of benzene was refluxed for 6 days under nitrogen. Prolonged reflux time is necessary to effect decarbonylation of the starting material. The light yellow solution was cooled and filtered under nitrogen. The filtrate was concentrated to approximately 5 ml with a stream of nitrogen and 10 ml of n-hexane was added. The crystals which formed were collected by filtration under nitrogen and washed with n-pentane. Recrystallization from a 1/5 benzene/n-hexane mixture yielded 0.43 g (90%) of light yellow crystals, m.p. 190–192°. (Found: C, 65.42; H, 4.94. $C_{30}H_{27}MnO_3P_2$ calcd.: C, 65.28; H, 4.93%.)

2,3-[*Bis(diphenylphosphino)methane*]-1-*methylmanganese tricarbonyl.* A procedure identical to that given above was followed in this preparation. A solution of 0.35 g (0.62 mol) of 2,3-$CH_3COMn(CO)_3[P(C_6H_5)_2CH_2P(C_6H_5)_2]$ yielded 0.31 g (93%) of light yellow crystals, m.p. 184–186°. (Found: C, 64.90; H, 4.62. $C_{29}H_{25}MnO_3P_2$ calcd.: C, 64.75; H, 4.68%.)

ACKNOWLEDGEMENTS

P. K. Maples gratefully acknowledges the receipt of a NASA Fellowship, 1964–1967, administered by Lehigh University. Funds provided by the NSF were used to purchase the ^1H NMR instrument.

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J. Organometal. Chem., 20 (1969) 269–272