

NOTE

SOME DISUBSTITUTED CARBONYL- π -CYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM

M. J. MAYS AND MISS S. M. PEARSON

University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)

(Received August 2nd, 1968)

We have previously described the preparation of complexes of formula $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{L}]_2\text{Hg}$ [$\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3$]¹. These air-stable complexes are useful intermediates in the synthesis of other phosphine-substituted derivatives and, for example, reduction with sodium amalgam followed by acidification is probably the optimum route to the hydride complexes, $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{L})\text{H}$, which are too unstable to withstand the forcing conditions required for direct substitution²⁻⁴. During the course of this work it was found that prolonged reflux (≥ 3 days) of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{Hg}$ with a large excess of $\text{P}(\text{OMe})_3$ in methylcyclohexane leads to more than one CO group per Mo atom being substituted. A complex of stoichiometry $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3[\text{P}(\text{OMe})_3]_3\text{Hg}$ can be crystallised from solution which we have shown by X-ray powder photography to be a distinct compound and not a 1/1 mixture of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{P}(\text{OMe})_3]_2\text{Hg}$ and the symmetrically disubstituted complex $\{\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{P}(\text{OMe})_3]_2\}_2\text{Hg}$. We therefore formulate it as $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{P}(\text{OMe})_3]\text{Hg}\{\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{P}(\text{OMe})_3]_2\}$; continuous reflux for several weeks does not effect further substitution of carbonyl groups.

Reduction of this complex with sodium amalgam presumably affords a 1/1 mixture of the mono- and disubstituted anions, since subsequent acidification or treatment with methyl iodide at room temperature, yields mixtures of the mono- and disubstituted hydride or methyl complexes respectively. These mixtures can be readily separated by chromatography and this method of preparation therefore provides a practicable route to these rather unstable disubstituted complexes. The methyl complex is a crystalline solid but the hydride is an oil which was not obtained analytically pure. Both these complexes decompose rapidly in air. The hydride was characterised by its IR and NMR spectra and by dissolving it in carbon tetrachloride to form the disubstituted chloride derivative which was more stable and could be analysed. We have also prepared the disubstituted trichlorotin complex by treatment of the chloride with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol and the iodide by shaking the mercury complex with iodine in CCl_4 . Analytical data on these new complexes are given in Table 1 together with some of their properties. Similar disubstituted halide complexes with other phosphines have been prepared previously by direct substitution²⁻⁴ but the other complexes are the first of their type. NMR spectra of the new complexes

TABLE I
COLOUR, YIELD, INFRARED SPECTRA AND ANALYTICAL DATA FOR NEW COMPLEXES

Compound	Colour	Yield ^a (%)	CO stretch (cm ⁻¹) ^b	Analysis found (calcd.) (%)				Mol. wt. found (calcd.)
				C	H	P	Cl	
$[C_3H_5Mo(CO)_2P(OMe)_3]_2Hg^-$ $-[C_3H_5Mo(CO)[P(OMe)_3]_2]$	Yellow	70	1970 w 1873 s 1810 vs 1833 vs	27.3 (27.0)	4.2 (3.8)	9.8 (9.5)		
$C_3H_5Mo(CO)[P(OMe)_3]_2H$	Colourless oil	20						
$C_3H_5Mo(CO)[P(OMe)_3]_2CH_3$	Yellow	50	1818 vs	34.3 (34.5)	5.5 (5.7)	13.2 (13.7)	400 (452)	
$C_3H_5Mo(CO)[P(OMe)_3]_2Cl$	Yellow	50	1829 vs	31.2 (30.5)	4.6 (4.8)	12.9 (13.1)	7.6 (7.5)	
$C_3H_5Mo(CO)[P(OMe)_3]_2SnCl_3$	Yellow- orange	40	1896 vs	22.0 (21.7)	3.2 (3.4)	15.9 (16.0)	660 (663)	
$C_3H_5Mo(CO)[P(OMe)_3]_2I$	Orange	60	1837 vs	25.7 (25.5)	3.7 (4.1)	11.0 (11.0)	540 (564)	

^a Yield of mercury derivative based on unsubstituted complex; other yields based on the substituted mercury complex. ^b Measured in chloroform solution.

TABLE 2
 NMR SPECTRA OF NEW COMPLEXES^a

Compound	C ₅ H ₅ (τ)	OCH ₃ (τ)	Other proton resonances (τ)
[C ₅ H ₅ Mo(CO) ₂ P(OMe) ₃]Hg-	4.94	6.36, 6.56 ^b ;	
-{C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ }		6.37, 6.57 ^c	
C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ H	4.80	6.32, 6.52	τ(MoH) 17.46 (triplet); J(P-H) 64.5 cps
C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ CH ₃	4.92	6.31, 6.41, 6.50 ^d	τ(MoCH ₃) 10.27 (triplet); J(P-CH ₃) 10.5 cps
C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ Cl	4.68	6.14, 6.23, 6.31 ^d	
C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ SnCl ₃	4.65	6.13, 6.33	
C ₅ H ₅ Mo(CO)[P(OMe) ₃] ₂ I	4.75	6.13, 6.22, 6.32 ^d	

^a Measured in CDCl₃. ^b Monosubstituted. ^c Disubstituted. ^d A triplet with a broad central component of differing relative height.

are presented in Table 2. Whilst the proton resonance of the P(OMe)₃ groups is a doublet for the hydride and trichlorotin compounds, triplets are observed for the chloride, iodide and methyl complexes. These triplets consist of a broad central line of differing height with respect to the two sharp outer lines. Spectra such as these are typical of an X_nAA'X'_n system⁵: in the case of the hydride and trichlorotin complexes the observation of a doublet means that |J(PMP')| is small compared to |J(POCH)-J(PMP'OCH)| while for the chloride, iodide and methyl complexes this is no longer true. It has been suggested⁵ that there is a strong correlation between the value of J(PMP') and the angle subtended at the metal atom by the two phosphorus atoms. This does not seem likely to be the only factor operating for our complexes, since it would be rather surprising that the hydride and trichlorotin ligands which have very different steric requirements give rise to one type of spectrum and the other ligands to a different type. Clearly a more detailed study is required before any general conclusions can be drawn. The C₅H₅ proton resonance is a singlet for all the complexes, including the mercury derivative which contains C₅H₅ groups in two different environments; it must be assumed that the resonances coincide.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 257 grating instrument and NMR spectra on a Perkin-Elmer R. 10 instrument at 60 Mc/sec. Molecular weights (dichloromethane) were determined using a vapour pressure osmometer at 37°. [π -C₅H₅Mo(CO)₃]₂Hg was prepared by the literature method⁶. All preparations, separations and purifications were carried out under nitrogen. Solvents were degassed before use.

[Tricarbonyltris(trimethylphosphite)di- π -cyclopentadienyldimolybdenum]mercury

[π -C₅H₅Mo(CO)₃]₂Hg (1.0 g) was refluxed with an excess of trimethyl phosphite (5 ml) in methylcyclohexane solution (3 days). On cooling, deep yellow crystals separated which were washed well with ethanol and dried *in vacuo*.

Hydridomonocarbonylbis(trimethylphosphite)- π -cyclopentadienylmolybdenum

$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3[\text{P}(\text{OMe})_3]_3\text{Hg}$ (1.0 g) was reduced by stirring with 1% Na/Hg in THF solution (100 ml) for 2 h. The solution was acidified with glacial acetic acid (3 ml) and then stirred for a further $\frac{1}{2}$ h. After removal of the solvent the residue was extracted with ether and the extract chromatographed on alumina. Two yellow bands were eluted by a 40/60 ether/hexane mixture. The first of these was identified as $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OMe})_3]\text{H}^1$. Evaporation of the second band gave the product as a colourless oil which decomposed instantly on exposure to air.

Methylmonocarbonylbis(trimethylphosphite)- π -cyclopentadienylmolybdenum

The reduced solution obtained as for the hydride was treated with methyl iodide and stirred for a further $\frac{1}{2}$ h. After removal of solvent, the residue was extracted with ether and the extract chromatographed on alumina. Two yellow bands were eluted with ether the first of which was identified as $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OMe})_3]\text{-CH}_3^1$. Evaporation of solvent from the second band left a pale yellow residue which was recrystallised twice from ether/hexane at -78° to give yellow crystals of the product.

Chloromonocarbonylbis(trimethylphosphite)- π -cyclopentadienylmolybdenum

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{P}(\text{OMe})_3]_2\text{H}$ (0.5 g) was dissolved in excess CCl_4 (100 ml) and left at room temperature for 2 days. Evaporation of solvent left a yellow residue which was extracted with a minimum of ether and chromatographed on alumina. Elution with ether afforded a yellow band from which yellow crystals of the product were obtained.

Trichloro[carbonylbis(trimethylphosphite)- π -cyclopentadienylmolybdenum]tin

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{P}(\text{OMe})_3]_2\text{Cl}$ (0.27 g) was refluxed with excess ($\times 10$) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.3 g) in A.R. methanol for 3 h. On cooling the solution, yellow-orange crystals of the product were obtained.

Iodomonomocarbonylbis(trimethylphosphite) π -cyclopentadienylmolybdenum

$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3[\text{P}(\text{OMe})_3]_3\text{Hg}$ (1 g) was dissolved in CH_2Cl_2 (10 ml) and treated with a solution of I_2 (0.5 g) in CCl_4 (100 ml) which was added slowly with shaking. The solution was left at room temperature for 12 h, and after evaporation of solvent, the orange residue was extracted with ether and chromatographed on alumina. Elution with ether gave an orange-red band followed by a paler orange band. The first band was identified as $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OMe})_3]\text{I}$, and evaporation of solvent from the second band gave an orange residue which was recrystallised from ether/hexane at -78° to give orange crystals of the product.

ACKNOWLEDGEMENT

We thank the Molybdenum Climax Company for a generous gift of molybdenum carbonyl. One of us (S.M.P.) thanks the S.R.C. for a studentship.

REFERENCES

- 1 M. J. MAYS AND S. M. PEARSON, *J. Chem. Soc., A*, (1968) 2291.
- 2 R. J. HAINES, R. S. NYHOLM AND M. H. B. STIDDARD, *J. Chem. Soc., A*, (1967) 94.
- 3 A. R. MANNING, *J. Chem. Soc., A*, (1967) 1984.
- 4 P. M. TREICHEL, K. W. BARNETT AND R. L. SHUBKIN, *J. Organometal. Chem.*, 7 (1967) 449.
- 5 A. PIDCOCK, *Chem. Commun.*, (1968) 92; R. K. HARRIS, *Can. J. Chem.*, 42 (1964) 2275.
- 6 E. O. FISCHER, W. HAFNER AND H. O. STAHL, *Z. Anorg. Allg. Chem.*, 282 (1955) 47.

J. Organometal. Chem., 15 (1968) 257-261