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REACTIONS OF THE ANION $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]^-$

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SUMMARY

The reactivity series $[(\pi\text{-}C_5H_5)W(CO)_3]^- > [(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]^- > [(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ has been established. The complexes *trans*-$(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)R_f$ [$R_f = 4\text{-}C_6F_3(CN)_2\text{-}1,2; 4\text{-}C_5F_4N$], and improved preparations of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)H$ and $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$, are described.

INTRODUCTION

Comparison of the reactivities of the anions $[Mn(CO)_5]^-$ and $[Mn(CO)_4(PPh_3)]^-$ towards unsaturated fluorocarbons shows that replacement of a carbonyl group by triphenylphosphine results in increased reactivity[1,2]. This greater nucleophilicity may be related to the increased electron density on the metal atom resulting from both better σ donor, and poorer π acceptor properties of the phosphine ligand. Recently, the reactivity of the anion $[(\pi\text{-}C_5H_5)W(CO)_3]^-$ has been shown[3] to be greater than that of the analogous molybdenum species in reactions with some fluorocarbons. We decided to compare these two anions with one containing a phosphine ligand, namely $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]^-$, both from the point of view of reactivity, and also to extend the range of known molybdenum fluorocarbon complexes.

Brief reports of the synthesis of this anion by sodium amalgam reduction of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)X$ (X = Cl[4], I[5]) have appeared, together with an account of its reactions with dimethyl sulphate, acyl chlorides, $(Ph_2I)BF_4$, and Ph_3SnCl. More recently, accounts[6] of the cleavage of $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$ with excess sodium amalgam have come to our attention during the course of this work. The related anions $[(\pi\text{-}C_5H_5)M(CO)_2P(OMe)_3]^-$ (M = Mo, W) have also been described[7].

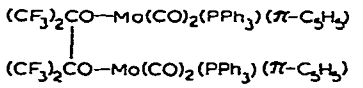
RESULTS AND DISCUSSION

We have found that a convenient route to the phosphine-substituted dimer, $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$, is the reaction between $Mo(CO)_3(PPh_3)_3$ and cyclopentadiene, in refluxing di-n-butyl ether. After short periods, a bright red solution, shown to contain the hydride, is formed. This initial product is formed by an oxidative-elimination reaction similar to that reported[8] with $Mo(CO)_3(MeCN)_3$. Continued refluxing of this solution then results in the formation of $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$, which separates as a microcrystalline solid in about 90% yield.

Treatment of this complex with excess sodium amalgam in the usual way, followed by reaction with fluorocarbon substrates, has given some indication of the reactivity of the resulting anion. Thus with pentafluoropyridine and with tetrafluorophthalodinitrile, complexes containing molybdenum σ-bonded to the fluorinated ring systems were readily formed. Previous experiments showed that $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ was insufficiently reactive to form a derivative with pentafluoropyridine[9]. With bromopentafluorobenzene, on the other hand, only the halide $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)Br$ was obtained, suggesting that $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]^-$ is a weaker nucleophile than $[(\pi\text{-}C_5H_5)W(CO)_3]^-$, which forms the pentafluorophenyltungsten complex with this reagent[3].

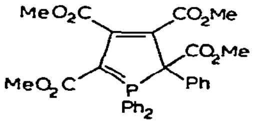
Acidification of solutions of the anion gave the hydride, $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)H$, which could also be obtained by interrupting the preparation of the dimer before separation of solid material. The identity of this material was confirmed from its infrared and proton NMR spectra [*e.g.* NMR (Bu_2O): τ 16.4, $J(P\text{-}H) \sim 50$ Hz; lit.[4] τ 15.5, $J(P\text{-}H)$ 51.6 Hz (in tetrahydrofuran)]. As expected, refluxing in chloroform gave a quantitative yield of the chloride, whilst treatment with iodine in tetrahydrofuran afforded the iodide.

The product from the reaction between the hydride and hexafluoroacetone was a yellow crystalline solid, analysing for $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(CF_3)_2CO$, and showing only one CF_3 resonance in its ^{19}F NMR spectrum. Solution molecular weights indicated that the complex was dimeric, and we suggest that the structure is (I). Dimerisation of hexafluoroacetone to the pinacol is known to occur readily, and formation of the complex follows.



$$\begin{array}{l}(CF_3)_2CO\text{—}Mo(CO)_2(PPh_3)(\pi\text{-}C_5H_5)\\ \quad | \\ (CF_3)_2CO\text{—}Mo(CO)_2(PPh_3)(\pi\text{-}C_5H_5)\end{array}$$

(I)



(II)

With hexafluoro-2-butyne, the product could not be separated from large amounts of waxy polymeric material also formed. With dimethyl acetylenedicarboxylate, the only compound isolated was the known phosphorane $Ph_3P[C_2(CO_2Me)_2]_2$, recently shown to have structure (II)[10].

Complexes of the type $(\pi\text{-}C_5H_5)Mo(CO)_2(PR_3)X$ can exist in *cis* or *trans* forms, which can be distinguished by physical methods, *e.g.* infrared[11] and proton NMR spectroscopy[12,13]. The fluorocarbon complexes described above show a $\nu(CO)$ intensity pattern corresponding to the *trans* isomer, and supporting this assignment is the appearance of the C_5H_5 resonance as a doublet. Only the phthalodinitrile derivative gave a well-resolved ^{19}F NMR spectrum, in which it was interesting to find that the fluorines *ortho* to the metal atom coupled with the phosphorus atom $[J(F\text{-}P) \sim 0.8$ Hz$]$. These resonances were quartets of doublets, in contrast to the signal at highest field, which was a simple quartet.

The spectrum of (I) showed four $\nu(CO)$ bands, a pair at 1973 and 1954 cm^{-1}, and a much more intense doublet at 1895 and 1872 cm^{-1}, suggesting the *trans* isomer.

The proton NMR spectrum, however, showed only a singlet resonance for the C_5H_5 group, so that we are unable to assign the stereochemistry of this complex unambiguously.

No mass spectra could be obtained for any of the complexes described herein. The only peaks to have significant intensities were those at *m/e* 278, 262, 183 and 152, commonly found in triphenylphosphine and its complexes, and probably arising from thermal decomposition in the source.

Several other attempts to obtain related phosphine or arsine–molybdenum complexes included (*i*) the reaction between $Mo(CO)_2(MeCN)_2(PPh_3)_2$ and cyclopentadiene, which gave a low yield of $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$; (*ii*) the reaction of $Mo(CO)_3(AsPh_3)_3$ with cyclopentadiene, which gave a deep red solution similar to that described for the PPh_3 complex, but which rapidly decomposed; (*iii*) the reaction of $Mo(CO)_3(PPh_3)_3$ with thallium cyclopentadienide. The last reaction gave a deep red solution, which afforded acetone-soluble dichroic red-green crystals on evaporation. This product is extremely air-sensitive, decomposing to a yellow material. It is probable that this product is the thallium(III) derivative, $Tl[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_3$, analogous to the complex $Tl[(\pi\text{-}C_5H_5)Mo(CO)_3]_3$ recently described by King[14].

EXPERIMENTAL

Spectra were recorded on Perkin–Elmer 257 (infrared), Varian Associates HA 100 (NMR) and GEC–AEI MS 902 (mass) instruments. Solvents were dried and distilled before use. All reactions were carried out under nitrogen.

Preparation of $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$

A mixture of freshly-distilled cyclopentadiene (15 ml) and the complex $Mo(CO)_3(PPh_3)_3$ (9.0 g) in di-n-butyl ether (100 ml) was stirred vigorously while refluxing. After 2.5 h, the solid material had dissolved to give a deep red solution (see p. 142). Continued heating then resulted in slow deposition of a bright red microcrystalline solid, which appeared to be complete after 48 h. After cooling, the solid was filtered, washed several times with ether, and dried, to give pure $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$ (4.0 g, 89%), m.p. 230–232° (lit.[11] 164°) (Found: C, 61.7; H, 4.2; Mo, 19.6; P, 6.2. $C_{50}H_{40}Mo_2O_4P_2$ calcd. C, 61.5; H, 4.1; Mo, 19.6; P, 6.3%.) Infrared: ν(CO); 1850 s, 1831 vs cm^{-1} (lit.[15]; 1853, 1830 cm^{-1}). Proton NMR spectrum: τ 2.7 m, br (C_6H_5); 5.54 d [C_5H_5, J(P–H) 1.5 Hz].

Reactions of the anion $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]^-$

A solution of the sodium salt of the complex anion was prepared by stirring $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_2$ (500 mg, 1.04 mmol) in tetrahydrofuran (25 ml) with an excess of sodium amalgam for 1.5 h. The initially insoluble red powder gradually turned yellow and dissolved to give a clear yellow solution, which was then freed of excess amalgam, and used for the reactions described below.

(*a*). *With pentafluoropyridine.* The anion solution was treated with pentafluoropyridine (200 mg, 1.18 mmol) and the mixture stirred for 1 h at room temperature. Filtration, removal of solvent, and crystallisation of the residue (ether) gave bright yellow crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)C_5F_4N$ (275 mg, 40%), m.p.

220–223° (dec.) (Found: C, 57.25; H, 3.4; F, 12.3; P, 5.2. $C_{30}H_{20}F_4MoNO_2P$ calcd.: C, 57.3; H, 3.2; F, 12.1; P, 4.9%.) Infrared: ν(CO); 1965s, 1870 vs (Nujol); 1971 s, 1886 vs cm^{-1} ($CHCl_3$). ^1H NMR: τ 2.51 m (C_6H_5); 5.16 d (C_5H_5, J 0.5 Hz); ^{19}F NMR: 100.0, 103.9 ppm (relative to $CFCl_3$ 0.0 ppm)

(*b*). *With tetrafluorophthalodinitrile.* A similar reaction using the dinitrile (300 mg, 1.5 mmol) afforded bright yellow crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}C_6F_3(CN)_2$ (200 mg, 30%) from an acetone/hexane mixture, m.p. 215° (Found: C, 60.6; H, 3.8. $C_{33}H_{20}F_3MoN_2O_2P$ calcd. C, 60.0; H, 3.1%.) Infrared: ν(CO); 1970 s, 1870 vs; ν(CN); 2240 m cm^{-1} ($CHCl_3$). ^1H NMR: τ 2.60 m (C_6H_5); 5.17 d (C_5H_5, J 0.8 Hz) ($CDCl_3$); ^{19}F NMR 59.8 dq [F(3)], 76.6 dq [F(5)], 135.2 q [F(6)] ppm; J(F(3)–P) 1.6, J(F(5)–P) 1.8, J(F(6)–P) 0, J_{35} 5.1, J_{36} 12.0, J_{56} 28.0 Hz.

(*c*). *With pentafluorobromobenzene.* Addition of C_6F_5Br (300 mg, 1.22 mmol) to the anion solution resulted in an immediate colour change from yellow to red, with the formation of a white precipitate. After filtration and evaporation, crystallisation of the oily residue (chloroform) gave bright red crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}Br$ (270 mg, 40%), identified by comparison with an authentic sample [ν(CO); 1970 s, 1882 vs (lit.[13] 1974, 1886 cm^{-1})].

A similar reaction with acetyl chloride gave $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl$, similarly identified.

Reactions of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)H$

The red solution obtained from the reaction between cyclopentadiene and $Mo(CO)_3(PPh_3)_3$ in refluxing di-n-butyl ether (after 2.5 h, see p. 141) contains the hydride, and reacted as follows:

(*a*). *With chloroform.* Addition of excess chloroform to the solution and refluxing for 1 h gave a pink precipitate. Recrystallisation ($CHCl_3$/ether) gave red crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl$ (98%), identified from its infrared spectrum [ν(CO); 1975 vs, 1884 vs (lit.[13] 1975, 1886 cm^{-1})].

(*b*). *With iodine.* A similar reaction with iodine in tetrahydrofuran also gave a pink precipitate, which was recrystallised (toluene/light petroleum) to give red crystals of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$ (55%), m.p. 230° (lit.[4] m.p. 225° dec.), identified from its infrared spectrum [ν(CO); 1970 vs, 1890 vs (lit.[13] 1971, 1892 cm^{-1})].

(*c*). *With hexafluoroacetone.* An excess of hexafluoroacetone was condensed into a solution of the hydride. On standing for three days at room temperature, large yellow crystals were deposited. Recrystallisation afforded bright yellow $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)OC(CF_3)_2]_2$, m.p. 217° (dec.) (Found: C, 54.5; H, 4.1; F, 18.2; P, 5.05% Mol. wt. (osmometric, CH_2Cl_2), 1048. $C_{56}H_{40}F_{12}Mo_2O_6P_2$ calcd.: C, 53.5; H, 3.2; F, 18.2; P, 4.8% Mol. wt., 1290.) Infrared: ν(CO); 1962 s, 1876 vs (Nujol); 1973 s, 1954 s, 1895 vs, 1872 vs cm^{-1} ($CHCl_3$). ^1H NMR: τ 2.72 m (C_6H_5); 5.03 s (C_5H_5) ($CDCl_3$). ^{19}F NMR: 83.2 s ppm.

Reaction between $Mo(CO)_3(PPh_3)_3$ *and thallium cyclopentadienide*

Equimolar proportions of $Mo(CO)_3(PPh_3)_3$ and thallium cyclopentadienide were refluxed in tetrahydrofuran for 20 h, to give a deep red solution. Filtration under nitrogen, evaporation of solvent, and extraction with acetone gave an extremely air-sensitive solution, which on treatment with hexane afforded dichroic green-red crystals. Consistent analyses could not be obtained, but suggested that the compound was $Tl[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)]_3$.

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REFERENCES

1 M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, 80 (1968) 835; *Angew. Chem., Int. Ed. Engl.*, 7 (1968) 747.
2 P. W. Jolly, M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.*, (1965) 5830.
3 M. I. Bruce, D. N. Sharrocks and F. G. A. Stone, *J. Chem. Soc. A*, (1970) 680.
4 A. R. Manning, *J. Chem. Soc. A*, (1968) 651.
5 E. S. Bolton, M. Dekker, G. R. Knox, and C. G. Robertson, *Chem. Ind.*, (1969) 327.
6 (a) A. N. Nesmeyanov, L. G. Makarova and N. A. Ustynyuk, *J. Organometal. Chem.*, 23 (1970) 517.
(b) M. D. Curtis, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 859.
7 M. J. Mays and S. M. Pearson, *J. Chem. Soc.*, (1968) 2291.
8 S. A. Keppie and M. F. Lappert, *J. Organometal. Chem.*, 19 (1969) P5.
9 J. Cooke, M. Green and F. G. A. Stone, *J. Chem. Soc. A*, (1968) 173.
10 N. E. Waite, J. C. Tebby, R. S. Ward and D. H. Williams, *J. Chem. Soc. C*, (1969) 1100.
11 A. R. Manning, *J. Chem. Soc. A*, (1967) 1984.
12 R. J. Mawby and G. Wright, *J. Organometal. Chem.*, 21 (1970) 169.
13 J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 92 (1970) 5852.
14 R. B. King, *Inorg. Chem.*, 9 (1970) 1936.
15 R. J. Haines, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc. A*,(1968) 43.