

Arene-Molybdenum Chemistry: Diprotonation of Arenetris(tertiary phosphine)molybdenum Compounds

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The compounds [(arene)Mo(PR₃)₃] [(I): arene = benzene, R = Et; arene = mesitylene (mst), R = Me] have been prepared. They are readily protonated by dilute aqueous acids forming the cations [(arene)Mo(PR₃)₃H]⁺, (II), and with concentrated aqueous acids further protonation gives [(arene)Mo(PR₃)₃H₂]²⁺, (III). Analogous diprotonated cations (arene = benzene, R₃ = Ph₂Me or PhMe₂) are also described.

We have shown that some bis(arene)molybdenum compounds undergo displacement of one arene ring with certain tertiary phosphines giving the compounds [(arene)Mo(PR₃)₃], (I).¹ We now describe further the chemistry of this system.

RESULTS

Treatment of bis(η-benzene)molybdenum with the trialkylphosphines Et₃P or Me₃P, under similar conditions to those producing substitution of a benzene ring of [(η-C₆H₆)₂Mo] by the phosphines PPh₂Me or PPhMe₂,¹ does not give the analogous reaction. However, the compounds

mediates [(arene)Mo(η-C₃H₅)(PR₃)Cl] have been isolated but normally this is not necessary in the preparation of compounds (I).

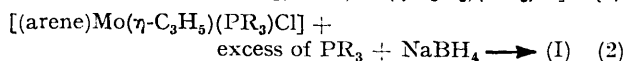
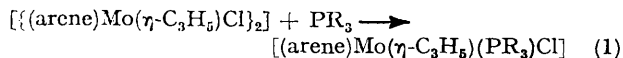
Evidence for the formulations of compounds (I) is given in the Table. The compounds are essentially similar to the previously described analogues (arene = benzene, R₃ = Ph₂Me or PhMe₂),¹ except the former are more soluble in benzene and light petroleum. Also compounds (I) are more readily oxidised by oxygen. Derivatives (I) appear to be rather more basic than the analogues (R₃ = Ph₂Me or PhMe₂) since they react with dilute acids giving the cations [(arene)Mo(PR₃)₃H]⁺, (II), and with stronger

Analytical and ¹H n.m.r. data

Compound	Colour	Analyses (%)			¹ H n.m.r. spectra ^a
		Found	Calc.		
[(η-C ₆ H ₆)Mo(PEt ₃) ₃]	Orange	54.6 (54.5)	10.1 (9.7)		6.27, 6, q (J ³¹ P-H 1.95), C ₆ H ₆ ; 8.4-9.4, 45, c, 9Et in C ₆ H ₆
[(mst)Mo(PMe ₃) ₃]	Orange	48.65 (48.7)	8.8 (8.9)	21.5 (21.0)	6.31, 3, q (J ³¹ P-H 2.3), C ₆ H ₆ ; 8.15, 9, s, Me ₃ C ₆ ; 8.98, 27, c, 9Me in C ₆ D ₆
[(η-C ₆ H ₆)Mo(PEt ₃) ₃ H]PF ₆ ^b	Yellow	42.6 (42.75)	7.7 (7.7)		5.25, 6, eight lines (J ³¹ P-H 4.10, J ¹ H-MoH 3.00), C ₆ H ₆ ; 7.7-9.4 5, c, 9Et; 11.75, 1, q (J ³¹ P-MoH 73.5), MoH in [² H ₆]Me ₂ CO
[(mst)Mo(PMe ₃) ₃ H]PF ₆	Red-violet	36.6 (36.6)	7.2 (6.8)		4.85, 3, s, C ₆ H ₆ ; 7.84, 9, s, Me ₃ C ₆ ; 8.40, 27, c, 9Me; 17.25, 1, q (J ¹ H- ³¹ P 52.2), H in [² H ₆]Me ₂ CO
[(η-C ₆ H ₆)Mo(PPh ₂ Me) ₃ H ₂][PF ₆] ₂	Yellow	50.2 (50.6)	4.5 (4.4)	14.1 (14.5)	2.50, 30, c, 6Ph; 4.05, 6, c, C ₆ H ₆ ; 7.95, 9, c, 3Me; 11.32, 2, q (J ³¹ P-H 43.5), 2H in CF ₃ CO ₂ H
[(η-C ₆ H ₆)Mo(PPhMe ₂) ₃ H ₂][PF ₆] ₂	Yellow	40.5 (40.9)	4.9 (4.7)	17.6 (17.5) ^d	2.60, 15, c, 3Ph; 4.22, 6, s (br), C ₆ H ₆ ; 8.40, 18, c, 6Me; 12.30, 2, q (J ³¹ P-H 43.5), 2H in CF ₃ CO ₂ H
[(η-C ₆ H ₆)Mo(PEt ₃) ₃ H ₂][PF ₆] ₂ ^e	Yellow	34.8 (35.1)	6.5 (6.5)	18.6 (18.8) ^f	3.75, 6, s (br), C ₆ H ₆ ; 7.5-9.2, 45, c, 9Et; 13.30, 2, q (J ³¹ P-H 43.5), 2H in CF ₃ CO ₂ H
[(mst)Mo(PMe ₃) ₃ H ₂][PF ₆] ₂ ^h	Yellow	29.7 (29.4)	6.2 (5.6)	19.3 (21.0)	3.76, 3, s (br), C ₆ H ₆ ; 7.42, 9, s, Me ₃ C ₆ ; 8.07, 27, c, 9Me; 13.34, 2, q (J ³¹ P-H 48.6), MoH ₂ in CF ₃ CO ₂ H

^a mst = mesitylene. Given as chemical shift (τ), relative intensity, multiplicity (J in Hz), assignment; *m/e* 412 for [(η-C₆H₆)⁹⁸-Mo(PEt₃)₃]⁺. ^b ν_{Mo-H} at 1 910 w cm⁻¹. ^c ν_{Mo-H} at 1 880 m cm⁻¹. ^d F 25.7 (25.9%). ^e ν_{Mo-H} at 1 910 w cm⁻¹. ^f F 27.5 (27.9%). ^g In liquid SO₂: room-temperature bands at 4.00, 6, s (br); 7.8-9.4, 45, c; and 13.60, 2, q (J 43.5); low-temperature (-70 °C) bands at 4.1, 6, s, C₆H₆; 7.8-9.4, 45, c, 9Et; 12.4, 1, q (br) (J³¹P_{a,b,c}-H_a 51), H_a; 15.3, 1, t (br) (J³¹P_{a,b,c}-H_b 48), H_b. ^h ν_{Mo-H} at 2 030 vw cm⁻¹.

[(arene)Mo(PR₃)₃] [(I): arene = benzene, R = Et; arene = mesitylene (mst), R = Me] may be prepared by an indirect route, as in equations (1) and (2). Some of the inter-

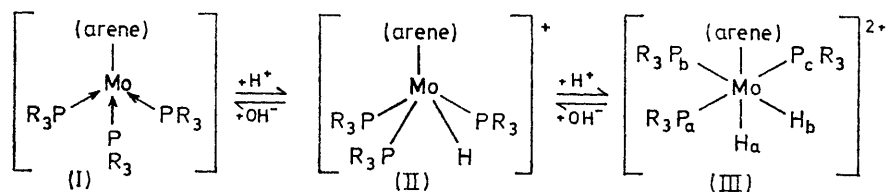


acids such as concentrated hydrochloric acid a further proton is added giving [(arene)Mo(PR₃)₃H₂]²⁺, (III). The analogues (I; arene = benzene, R₃ = Ph₂Me or PhMe₂) only give the corresponding monoprotinated cations (II), when treated with concentrated hydrochloric acid, as described previously.¹ However, in stronger acid media,

¹ M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc. (A)*, 1971, 2929.

namely in pure trifluoroacetic acid, these cations also undergo further protonation giving (III).

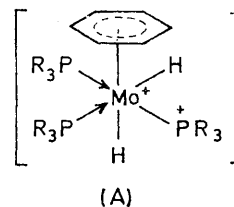
The new cations (II) and cations (III) were isolated and characterised as hexafluorophosphate salts. Evidence for



this formulation is provided by analysis, i.r., and, especially, ^1H n.m.r. data given in the Table. The ^1H n.m.r. spectrum of compound (III; $\text{R} = \text{Et}$) at room temperature was essentially the same in both pure trifluoroacetic acid and liquid sulphur dioxide. At room temperature the band assigned to the MoH_2 system appeared as a quartet (τ 13.6), so that the two hydrogen and three phosphine ligands appear to be equivalent. Lowering the temperature caused the quartet to collapse and at -70°C a new quartet (τ 12.4, J 51 Hz) and broad triplet (τ 15.3, J 48 Hz) appeared. The two bands were of approximately equal intensity. On warming to room temperature the original quartet reappeared. The low-temperature spectrum indicates either that two isomers are present in approximately equal proportions or, more probably, there is a diprotonated form with non-equivalent hydrogens. Compounds (III) all lost a proton in acetone solution giving compounds (II). The mono- and di-protonated compounds were readily deprotonated on treatment with ethanolic sodium hydroxide solution giving the corresponding neutral compounds (I).

DISCUSSION

The addition of a proton to neutral transition-metal compounds giving hydrido-cations has been long established. For example, (arene)tricarboxylchromium compounds add one proton in strong-acid mixtures such as $\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{CO}_2\text{H}$ and it was suggested that the basicity of the chromium compounds is increased with increasing methyl substitution of the arene ring.² It is, therefore, not surprising that the compounds [(arene) $\text{Mo}(\text{PR}_3)_3$] are much more basic than the [(arene) $\text{Cr}(\text{CO})_3$] analogues since tertiary phosphines are much less efficient in removing electron density from the metal atom than the carbon monoxide ligand. Nonetheless, successive addition of two protons to molybdenum in compounds (I) to yield the doubly charged cations (III) is unusual. Indeed, we believe there are no other examples where two protons have been added to the same atom in a neutral molecule, giving an isolable cation. It seems that the ability of the molybdenum centre in compounds (I) to undergo diprotonation reflects unusually high electron density on the metal atom, together with a marked ability to delocalise positive charge. A reasonable mechanism of charge delocalisation on to the phosphorus atoms is illustrated by structure (A), for



which there are two alternatives in which the other phosphorus atoms are quaternised.

The variable-temperature ^1H n.m.r. spectrum of compound (III; $\text{R} = \text{Et}$) very closely resembles that

recently observed for $\text{cis-}[\text{H}_2\text{Fe}(\text{PPh}_2\text{Et})_3\text{CO}]$.³ By analogy we propose that the compounds (III) have a similar structure with a cis-MoH_2 system and two

equivalent and one unique phosphorus ligands. Further studies on this fluxional system are in progress.

EXPERIMENTAL

All preparations and reactions were carried out in the absence of oxygen and, where indicated, argon was preferred as the inert atmosphere. Where necessary, solvents were dried by heating under reflux over, and distillation from, calcium hydride. I.r. spectra were determined on mulls using a Perkin-Elmer 457 spectrometer. ^1H N.m.r. spectra were determined on a Japan Electron Optics instrument operating at 60 MHz. The compounds [(arene)- $\text{Mo}(\eta\text{-C}_3\text{H}_5\text{Cl})_2$] were prepared as previously described.⁴

Preparation of Complexes.—(η -Benzene)tris(triethylphosphine)molybdenum. The dimer [($\eta\text{-C}_6\text{H}_6$) $\text{Mo}(\eta\text{-C}_3\text{H}_5\text{Cl})_2$] (0.5 g, 1.0 mmol) in ethanol (15 cm^3) under an argon atmosphere was treated with triethylphosphine (0.3 cm^3 , 2.0 mmol) and the mixture was stirred at 70°C for 30 min. The resulting deep red solution was cooled to room temperature, then water (3 cm^3), triethylphosphine (0.9 cm^3 , 6.0 mmol), and sodium tetrahydroborate (1.0 g) were added. The mixture was stirred at room temperature for 2 h and a yellow solid appeared. The solution was filtered giving a yellow solid and a filtrate (a). The yellow solid was extracted with light petroleum, the extract filtered, and the dark yellow filtrate cooled slowly to -60°C giving yellow-orange needles. The filtrate (a) was kept at room temperature for 3 days when orange crystals appeared which were separated by filtration from a pale red filtrate (b). The orange crystals were recrystallised from light petroleum, as described above. The filtrate was kept at room temperature for 7 days and more orange solid separated which was then recrystallised from light petroleum. The orange products were combined and recrystallised from light petroleum at -60°C giving the pure compound which was dried *in vacuo*, yield 42%.

² A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.

³ P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 75.

⁴ M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

(η -Mesitylene)tris(trimethylphosphine)molybdenum. The finely ground compound $[(\text{mst})\text{Mo}(\eta\text{-C}_3\text{H}_5\text{Cl})_2]$ (1 g) in ethanol (95%, 50 cm³) was treated with trimethylphosphine (1 cm³) for 6 h under reflux and in an argon atmosphere. An excess of powdered sodium tetrahydroborate (1 g) was then added and the resulting solution stirred at room temperature for 5 days. Water (100 cm³) was then added to the orange-red solution and orange crystals separated over a period of 7 days. The crystals were collected, dried, and extracted with cold light petroleum (50 cm³). After filtration the filtrate was concentrated under reduced pressure (to 10 cm³) and cooled (to -78 °C). Orange crystals separated which were washed with a little cold petroleum and dried *in vacuo* giving the pure compound, yield 0.6 g.

(η -Benzene)hydrogentris(triethylphosphine)molybdenum hexafluorophosphate. The compound $[(\eta\text{-C}_6\text{H}_6)\text{Mo}(\text{PET}_3)_3]$ (0.5 g) was treated with ethanol (5 cm³) and hydrochloric acid (2N; 5 cm³). The mixture was stirred at 50 °C for 10 min. Excess of aqueous ammonium hexafluorophosphate was added giving a pale yellow precipitate which was collected, washed with water (3 × 5 cm³), and dried *in vacuo*. The product was recrystallised from dichloromethane-diethyl ether and finally dried *in vacuo*, yield ca. 90%.

Hydrogen(η -mesitylene)tris(trimethylphosphine)molybdenum hexafluorophosphate. The compound $[(\text{mst})\text{Mo}(\text{PMe}_3)_3]$ (0.1 g) in dioxan (15 cm³) and water (2 cm³) was treated with hydrochloric acid (0.5N). The violet solution was filtered and aqueous ammonium hexafluorophosphate added. Violet crystals separated which were collected and recrystallised from acetone-water and finally dried *in vacuo* giving the pure compound, 0.05 g.

(η -Benzene)dihydrogentris(dimethylphenylphosphine)molyb-

denum hexafluorophosphate. Tris(dimethylphenylphosphine)molybdenum (0.58 g, 1.0 mmol) in pure trifluoroacetic acid (5 cm³) was treated with hexafluorophosphoric acid (65%, 2 cm³). The solution was concentrated under reduced pressure giving yellow microcrystals. After filtration the residue was washed with water (3 × 3 cm³) and dried *in vacuo*, ca. 75% yield.

(η -Benzene)dihydrogentris(triethylphosphine)molybdenum hexafluorophosphate. A suspension of (η -benzene)tris(triethylphosphine)molybdenum (0.52 g, 1.0 mmol) in water (5 cm³) under an argon atmosphere was treated with concentrated hydrochloric acid (5 cm³). The mixture was stirred for 5 min giving a yellow solution which was filtered and a few drops of saturated aqueous ammonium hexafluorophosphate added. Yellow microcrystals precipitated which were collected, washed with water (3 × 5 cm³), and finally dried *in vacuo*, ca. 90% yield. The analogue $[(\text{mst})\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{PF}_6]_2$ was similarly prepared.

Dihydrogen(η -mesitylene)tris(trimethylphosphine)molybdenum bis(hexafluorophosphate). The pure compound $[(\text{mst})\text{Mo}(\text{PMe}_3)_3]$ (0.2 g) in ethanol (95%, 25 cm³) was treated with concentrated hydrochloric acid (0.5 cm³). The solvent was removed under reduced pressure and the residue extracted with water (10 cm³). The red-orange extract was treated with concentrated hydrochloric acid (2 cm³) and the solution became yellow. Saturated aqueous ammonium hexafluorophosphate was added precipitating a yellow solid which was collected, washed with water, and dried *in vacuo* giving the pure compound, yield 0.265 g.

We thank the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

[3/2273 Received, 5th November, 1973]