Mono(cyclopentadienyl)molybdenum Chemistry: Hydrido-, Halogeno-, Allylic, and Butadiene Derivatives of [1,2-Bis(diphenylphosphino)ethane]-(η-cyclopentadienyl)molybdenum and Related Compounds

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The new compounds $[Mo(\eta\text{-}C_5H_5)_2L_2][PF_6]_2$, $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(dppe)]$, $[Mo(\eta\text{-}C_5H_5)L_2Cl_3]$, $[Mo(\eta\text{-}C_5H_5)(dppe)H_3]$, $[Mo(\eta\text{-}C_5H_5)(dppe)Br_3].C_6H_5Me$, $[Mo(\eta\text{-}C_5H_5)_2(NCMe)_2][PF_6]_2$, $[Mo(\eta\text{-}C_5H_5)_2(dppm)H][PF_6]$, $[Mo(\eta\text{-}C_5H_5)(dppm)Cl][PF_6].0.5CH_2Cl_2$, and $[Mo(\eta\text{-}C_5H_5)(\mathit{exo}\text{-}H\text{-}C_5H_5)(dppe)][PF_6].CH_2Cl_2$ [L_2 = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm)] have been prepared. The trihydride $[Mo(\eta\text{-}C_5H_5)(dppe)H_3]$ reacts with butadiene giving $[Mo(\eta\text{-}C_5H_5)(dppe)(\eta^3\text{-}C_3H_4Me)]$.

THE compounds $[M(\eta\text{-}C_5H_5)_2H_3]$ (M = Nb or Ta) and $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) have an extensive chemistry and the bis(cyclopentadienyl) derivatives of these metals give rise, *inter alia*, to C–H activation,[1] simple carbene systems,[2,3] metallacyclobutane [4] derivatives, and other compounds of current interest. We wished to extend further these areas of chemistry and towards this end set out to prepare and study the chemistry of the system $[Mo(\eta\text{-}C_5H_5)(dppe)]$ [where dppe represents 1,2-bis(diphenylphosphino)ethane], which is isoelectronic with $Nb(C_5H_5)_2$.

Here we describe the synthesis of derivatives of the $[Mo(\eta\text{-}C_5H_5)(dppe)]$ system.

RESULTS

Chemical Studies.—Treatment of the di-iodo-compound $[Mo(\eta\text{-}C_5H_5)_2I_2]$ with thallium hexafluorophosphate and dppe gives the compound $[Mo(\eta\text{-}C_5H_5)_2(dppe)][PF_6]_2$ (1) in variable yields. Addition of dppe to acetone solutions of the trihydrido-cation $[Mo(\eta\text{-}C_5H_5)_2H_3]^+$ gives (1) and a yellow compound (2) of stoicheiometry $C_{36}H_{35}F_6MoP_3$. The relative yields of (1) and (2) vary with the temperature of the reaction. Maximum and satisfactory yields of (1) are found at lower temperatures.

Treatment of (1) with $Na[BH_4]$ in acetone followed by crystallisation from dichloromethane gives the 1—4-η-cyclopentadiene derivative $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_6)(dppe)][PF_6]\cdot CH_2Cl_2$ (3). This compound reacts with the triphenylmethyl cation reforming (1).

Treatment of (1) in acetone with $Na[BD_4]$ gives the deuterio-analogue of (3), namely $[Mo(\eta\text{-}C_5H_5)(C_5H_5D)(dppe)][PF_6]\cdot CH_2Cl_2$ (3d). The i.r. spectrum of (3) shows a band at 2 770 cm^{-1} which may be assigned to an *exo*-C–H stretch of the cyclopentadiene group. This band is absent in the spectrum of (3d), as would be expected, and the spectrum shows new bands at 2 060 and 2 090 cm^{-1} which may be assigned to the *exo*-C–D stretch. We deduce that hydride addition to (1) proceeds by *exo* attack as would be expected.

When (1) or (3) are treated with excess of $Na[BH_4]$ or $Na[AlH_2(OCH_2CH_2OMe)_2]$ in tetrahydrofuran (thf) the 1—3-η-cyclopentenyl derivative $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(dppe)]$, (4) is formed. Treatment of (4) with hydrogen chloride gives red crystals of the trichloro-derivative $[Mo(\eta\text{-}C_5H_5)(dppe)Cl_3]$ (5), and examination of the volatile components of the reaction mixture showed cyclopentene to be present (g.l.c.). Compound (5) reacts with $Na[AlH_2(OCH_2CH_2OMe)_2]$ forming the yellow hydride $[Mo(\eta\text{-}C_5H_5)(dppe)H_3]$ (6). The ^1H n.m.r. spectrum of (6) shows the hydrogens to be equivalent and it is to be presumed that the hydrogen ligands undergo rapid rearrangement on the time scale of the experiment.

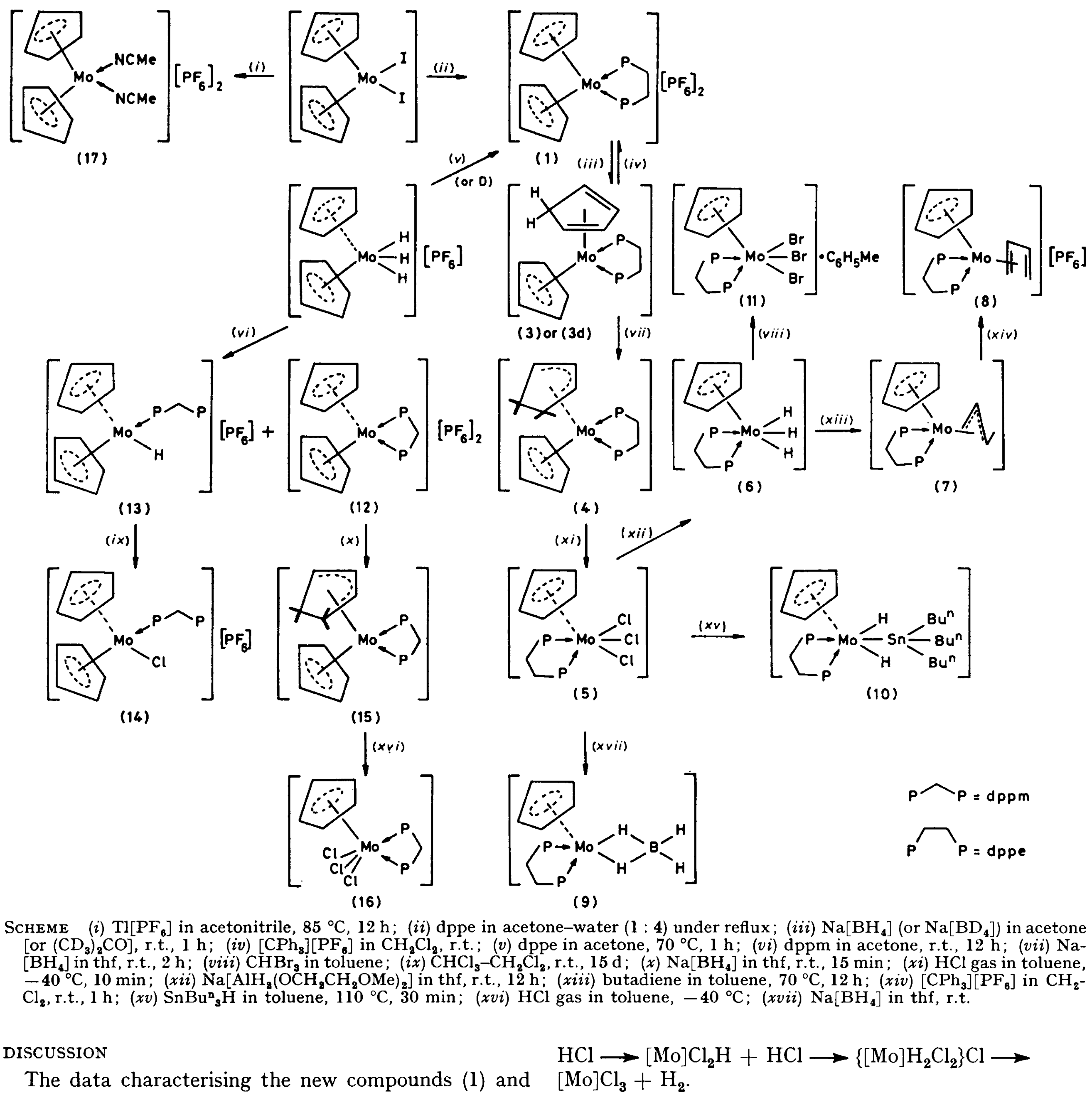
The trihydrido-derivative (6) reacts readily with butadiene giving the previously described isomers of the compound $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3H_4Me)(dppe)]$ (7). Treatment of (7) with the triphenylmethyl cation gives the known butadiene compounds $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_4H_6)(dppe)][PF_6]$ (8).[5]

During the development of the synthesis of (6) the reactions between (5) and $Na[BH_4]$ and $SnBu^n{}_3H$ were studied. The former gives a mixture of (6) and in small yield some green crystals which the spectroscopic data suggest to be the tetrahydroborato-derivative $[Mo(\eta\text{-}C_5H_5)(dppe)(BH_4)]$, (9). It was not possible to separate (9) completely from (6) by crystallisation and (9) decomposed on chromatography columns. The product from the tin reagent appears to be the yellow semi-crystalline compound $[Mo(\eta\text{-}C_5H_5)(dppe)H_2(SnBu^n{}_3)]$ (10).

Treatment of the trihydride (6) in toluene with bromoform gives the tribromide $[Mo(\eta\text{-}C_5H_5)(dppe)Br_3]\cdot C_6H_5Me$ (11).

We were interested to explore whether the bis(diphenylphosphino)methane (dppm) compound $[Mo(\eta\text{-}C_5H_5)(dppm)Cl_3]$ would be more readily accessible than the dppe analogue (5). Treatment of $[Mo(\eta\text{-}C_5H_5)_2H_3][PF_6]$ in acetone with dppm gives two products, namely $[Mo(\eta\text{-}C_5H_5)_2(dppm)][PF_6]_2$ (12), and $[Mo(\eta\text{-}C_5H_5)_2(dppm)H][PF_6]$ (13). Compound (13) reacts with chloroform in dichloromethane giving the chloro-derivative $[Mo(\eta\text{-}C_5H_5)_2(dppm)Cl][PF_6]\cdot CH_2Cl_2$ (14). Treatment of (13) with excess of $Na[BH_4]$ gives the expected 1—3-η-cyclopentenyl compound $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(dppm)]$ (15). Hydrogen chloride readily removes the cyclopentenyl group from the metal giving the trichloride $[Mo(\eta\text{-}C_5H_5)(dppm)Cl_3]$ (16). The preparation of (16) was not more convenient than for the compound (6) so work on the dppm system was discontinued.

We also report that the compound $[Mo(\eta\text{-}C_5H_5)_2(NCMe)_2][PF_6]_2$ (17) is readily prepared by treatment of $[Mo(\eta\text{-}C_5H_5)_2I_2]$ with acetonitrile. Reaction of (17) with $Na[BH_4]$ does not give rise to addition of hydride to the η-C_5H_5 ring, instead the acetonitrile ligands are displaced giving $[Mo(\eta\text{-}C_5H_5)_2H_2]$.



SCHEME (*i*) $Tl[PF_6]$ in acetonitrile, 85 °C, 12 h; (*ii*) dppe in acetone–water (1 : 4) under reflux; (*iii*) $Na[BH_4]$ (or $Na[BD_4]$) in acetone [or $(CD_3)_2CO$], r.t., 1 h; (*iv*) $[CPh_3][PF_6]$ in CH_2Cl_2, r.t.; (*v*) dppe in acetone, 70 °C, 1 h; (*vi*) dppm in acetone, r.t., 12 h; (*vii*) $Na[BH_4]$ in thf, r.t., 2 h; (*viii*) $CHBr_3$ in toluene; (*ix*) $CHCl_3$–CH_2Cl_2, r.t., 15 d; (*x*) $Na[BH_4]$ in thf, r.t., 15 min; (*xi*) HCl gas in toluene, −40 °C, 10 min; (*xii*) $Na[AlH_2(OCH_2CH_2OMe)_2]$ in thf, r.t., 12 h; (*xiii*) butadiene in toluene, 70 °C, 12 h; (*xiv*) $[CPh_3][PF_6]$ in CH_2Cl_2, r.t., 1 h; (*xv*) $SnBu^n{}_3H$ in toluene, 110 °C, 30 min; (*xvi*) HCl gas in toluene, −40 °C; (*xvii*) $Na[BH_4]$ in thf, r.t.

DISCUSSION

The data characterising the new compounds (1) and (3)—(17) are presented in the Table and require no further comment. The nature of the compound (2) will be discussed elsewhere.

The formation of (4) by successive addition of two hydride ions to the dication (1) follows the rules that we have recently formulated concerning regiospecific addition of nucleophiles to organometallic cations.[6] Indeed the synthesis of (4) was predicted on this basis. The reaction of (4) with hydrogen chloride was expected to give $[Mo(\eta\text{-}C_5H_5)(dppe)HCl_2]$ and (5) was not the anticipated product. We presume that the formation of (5) proceeds *via* the following sequence {where [Mo] represents $[Mo(\eta\text{-}C_5H_5)(dppe)]$}: $[Mo](\eta^3\text{-}C_5H_7) + HCl \longrightarrow [Mo](\eta^2\text{-}C_5H_8)Cl \longrightarrow [Mo]Cl + C_5H_8$; $[Mo]Cl + HCl \longrightarrow [Mo]Cl_2H + HCl \longrightarrow \{[Mo]H_2Cl_2\}Cl \longrightarrow [Mo]Cl_3 + H_2$.

The desired compound (6) was prepared in order to compare its reactivity with the isolectronic $[Nb(\eta\text{-}C_5H_5)_2H_3]$.[7] We find that (6) does not readily lose dihydrogen on heating nor will it catalyse exchanges between H_2 and C_6D_6. The reaction of (6) with butadiene forming the 1—3-η-methylallyl derivatives (7) parallels the reaction of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ with butadiene giving $[Nb(\eta\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_4Me)]$.[8] The analogue of the cation (8), namely $[Nb(\eta\text{-}C_5H_5)(\eta\text{-}C_4H_6)]^+$, has not been described. The bis(cyclopentadienyl)niobium system shows a marked tendency to form stable 17-electron compounds such as $[Nb(\eta\text{-}C_5H_5)_2R_2]$ (R = Cl or Me).[9] However, the analogous 17-electron systems $[Mo(\eta\text{-}C_5H_5)(dppe)R_2]$ were not observed during our studies.

Analytical and spectroscopic data

	Compound	Colour	Analysis (%) [a]		Selected i.r. data (cm^{-1}) [b]	^{1}H N.m.r. data [c]
			C	H		
(1)	$[Mo(\eta\text{-}C_5H_5)_2(dppe)][PF_6]_2$	Yellow	47.0 (47.3)	3.7 (3.7)		2.0—2.53, **20**, *c*, Ph; 4.28, **10**, *t* [*J*(P–H) 2.13], C_5H_5; 6.08, **4**, m, PCH_2CH_2P [d]
(2)	$[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)(dppe)][PF_6]_2\cdot CH_2Cl_2$	Yellow	54.4 (54.0)	4.5 (4.3)		
(3)	$[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)(dppe)][PF_6]\cdot CH_2Cl_2$	Yellow	52.2 (51.9)	4.9 (4.4)	$\nu(CH)_{exo}$ 2 770	2.2—3.3, **20**, *c*, Ph; 4.54, **2**, *s*, CH_2Cl_2; 5.13, **5**, *t* [*J*(P–H) 1.2], C_5H_5; 5.32, **2**, *d* (*J* 11.9), $H_A,H_{A'}$; 6.42, **1**, *d* (*J* 12.01), H_{exo}; 6.8, **6**, *c*, $H_B,H_{B'}$, PCH_2CH_2P; 7.49, **1**, *d* (*J* 12.01), H_{endo} [e,f]
(3d)	$[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_5D)(dppe)][PF_6]\cdot CH_2Cl_2$	Yellow			$\nu(CD)_{exo}$ 2 060, 2 090	2.2—3.2, **20**, *c*, Ph; 4.54, **2**, *s*, CH_2Cl_2; 5.13, **5**, *t* [*J*(P–H) 1.2], C_5H_5; 5.32, **2**, *d*, H_A, $H_{A'}$; 6.82, **6**, *c*, PCH_2CH_2P, H_B, $H_{B'}$; 7.49, **1**, *br s*, H_{endo} [e]
(4)	$[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(dppe)]$	Yellow-orange	68.8 (69.0)	5.7 (5.8) [g]		2.4—3.2, **20—25**, *c*, Ph; 5.53, **5**, *t* [*J*(P–H) 0.67], C_5H_5; 7.5—8.7, **11—12**, *c*, PCH$_2$CHP, C_5H_7 [h]
(5)	$[Mo(\eta\text{-}C_5H_5)(dppe)Cl_3]\cdot MeOH$	Red	55.3 (55.1)	5.1 (4.7) [i]		2.2—2.9, **20**, *c*, Ph; 4.98, **5**, *t* [*J*(P–H) 4] C_5H_5; 6.73, **3**, *s*, MeOH; 6.78; **4**, *br*, PCH_2CH_2P [e]
(6)	$[Mo(\eta\text{-}C_5H_5)(dppe)H_3]$	Yellow	66.7 (66.2)	5.9 (5.7)	ν(MoH) 1 800, 1 780	3.05—2.6, **20**, *c*, Ph; 5.65, **5**, *s*, C_5H_5; 7.75, **4**, *c*, PCH_2CH_2P; 25.15, **3**, *t* [*J*(P–H) 3.8], MoH_3 [h]
(9)	$[Mo(\eta\text{-}C_5H_5)(dppe)(BH_4)]$	Green	See text		$\nu(BH_4)$ 2 418, 2 390, 2 318	3.0—2.65, **20**, *c*, Ph; 5.45, **5**, s, C_5H_5; 7.95—7.35, **4**, *c*, PCH_2CH_2P, 37.15, *ca.* **4**, *br*, BH_4 [h]
(10)	$[Mo(\eta\text{-}C_5H_5)(dppe)H_2(SnBu^n{}_3)]$	Yellow			ν(MoH) 1 815	3.3—2.2, **20**, *c*, Ph; 5.95, **5**, *t* [*J*(P–H) 1.5], C_5H_5; 9.37—7.87, **31**, *c*, Bu^n, PCH_2CH_2P; 16.15, **2**, *t* [*J*(P–H) 36], Mo–H_2 [h]
(11)	$[Mo(\eta\text{-}C_5H_5)(dppe)Br_3]\cdot C_5H_5Me$	Red	49.7 (51.2)	4.2 (4.2) [k]		1.77—3.22, *ca.* **20**, *c*, Ph; 2.89, **5**, *s*, Ph (toluene); 5.52, **5**, *br t* [*J*(P–H) 1.5], C_5H_5; 7.7, **3**, *s*, Me (toluene); 7.62—8.32, *ca.* **4**, *c*, PCH_2CH_2P [l]
(12)	$[Mo(\eta\text{-}C_5H_5)_2(dppm)][PF_6]_2$	Orange	46.6 (46.7)	3.5 (3.6)		2.60—2.05, **20**, *c*, Ph; 3.66, **2**, *t* [*J*(P–H) 12], PCH_2P; 6.32, **10**, *t* [*J*(P–H) 2.0], C_5H_5 [d]
(13)	$[Mo(\eta\text{-}C_5H_5)_2(dppm)H][PF_6]$	Yellow	55.3 (55.6)	4.7 (4.4)	ν(Mo–H) 1 890	1.85—2.4, **20**, *c*, Ph; 4.43, **10**, *d* [*J*(P–H) 2.2], C_5H_5; 6.05, **2**, *d* [*J*(P–H) 9], PCH_2P; 17.84, **1**, *d* [*J*(P–H) 36], Mo–H [d]
(14)	$[Mo(\eta\text{-}C_5H_5)_2(dppm)Cl][PF_6]\cdot 0.5CH_2Cl_2$	Purple	51.1 (51.2)	3.8 (4.0) [m]		2.9—2.45, **20**, *c*, Ph; 4.3, **1**, *s*, CH_2Cl_2; 4.39, **10**, *d* [*J*(P–C_5H_5) 0.67], C_5H_5; 6.18, **2**, *d* [*J*(P–CH_2) 8], PCH_2P
(15)	$[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(dppm)]$	Orange	69.9 (68.6)	5.9 (5.6)		2.74, **20**, *c*, Ph; 5.30, **5**, *t* [*J*(P–C_5H_5) 1.05], C_5H_5; 7.14—9.04, **9**, *c*, PCH_2CH_2P, C_5H_7 [n]
(16)	$[Mo(\eta\text{-}C_5H_5)(dppm)Cl_3]$	Purple	54.8 (55.3)	4.4 (4.1)		2.93—2.23, ~**20**, *c*, Ph; 4.98, **5**, *s*, C_5H_5; 5.48, **2**, *t* [*J*(P–CH_2) 9], PCH_2P [l]
(17)	$[Mo(\eta\text{-}C_5H_5)_2(NCMe)_2][PF_6]_2$	Red	28.5 (28.1)	2.7 (2.7) [o]	ν(CN), 2 325, 2 300	4.02, **10**, *s*, C_5H_5; 7.6, **6**, *s*, Me_2 [p]

In (3) and (3d) the cyclopentadiene-ring protons are labelled as follows: $\overline{\mathrm{CH_2CH_BCH_ACH_{A'}C}}\mathrm{H_{B'}}$.

[a] Calculated values are given in parentheses. [b] Nujol mulls [c] Given as: chemical shift (τ), **relative intensity**, *multiplicity* (*J* in Hz), assignment. [d] In $(CD_3)_2CO$. [e] In CD_3CN. [f] Phosphorus-31 n.m.r. spectrum in CD_3CN: 86.14, *s*, PCH_2CH_2P; −144, **66**, *septet* [*J*(P–F) 705.63 Hz],$[PF_6]^-$. Relative to H_3PO_4 as external standard. [g] Mass spectrum: *m/e* 628, *P* for ^{98}Mo. [h] In C_6D_6. [i] Mo, 14.4 (13.8)%. [j] Mass spectrum shows highest peak at *m/e* 722 corresponding to $[^{98}Mo(\eta\text{-}C_5H_5)(dppe)^{118}(SnBu^n)]^+$; carbon and hydrogen analyses were high due to trace amounts of solvent in the waxy solid. [k] Br, 24.8 (26.9)%. [l] In $CDCl_3$. [m] Cl, 9.0 (8.7)%. [n] In $C_6D_5CD_3$. [o] N, 5.0 (4.7)%. [p] In SO_2.

We conclude that the system $[Mo(\eta\text{-}C_5H_5)(dppe)]$ differs substantially in its reactivity from that of the $Nb(\eta\text{-}C_5H_5)_2$ system.

EXPERIMENTAL

All reactions and manipulations were carried out under dinitrogen or *in vacuo*. All solvents were dried and distilled. Hydrogen-1 n.m.r. spectra were determined using a Bruker (90 MHz) or JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical department of this laboratory. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Mass spectra were determined using an A.E.I. M.S.9 spectrometer.

[1,2-*Bis(diphenylphosphino)ethane*]*bis*(η-*cyclopentadienyl*)-*molybdenum Bis*(*hexafluorophosphate*) (1).—*Method A*. The compound $[Mo(\eta\text{-}C_5H_5)_2Br_2]$ [10] (8.20 g, 21.2 mmol) and dppe (18.5 g, 21.2 mmol) in acetone (1 000 cm^3) were stirred at 60 °C and the suspension was treated in a slow dropwise manner with a suspension of Tl[PF$_6$] (7.4 g, 21.2 mmol) in acetone (600 cm^3) over 12 h. The reaction mixture was stirred for another 6 h. A suspension of Tl[PF$_6$] (7.4 g, 21.2 mmol) in acetone (600 cm^3) was then added over 12 h, giving a yellow solution. This was filtered and the solvent removed under reduced pressure. The residual yellow solid was washed with water (3 × 50 cm^3) and toluene (3 × 50 cm^3) and extracted with acetone–methanol (1 : 1). The extract was filtered and concentrated giving yellow *crystals* of $[Mo(\eta\text{-}C_5H_5)_2(dppe)][PF_6]_2$. These were washed with methanol and dried *in vacuo*, yield 11.6 g (60%). However, yields from this route were found to be unreliable, and the following improved method was adopted.

Method B. The compound $[Mo(\eta\text{-}C_5H_5)_2H_2]$ [11] (2 g, 8.77 mmol) was dissolved in dilute aqueous HCl (1 : 10) and the solution was treated with [NH$_4$][PF$_6$] (1.47 g, 9.0 mmol) giving a bulky white precipitate of $[Mo(\eta\text{-}C_5H_5)_2H_3][PF_6]$. This was washed with water (2 × 50 cm^3), dried, and then dissolved in acetone (50 cm^3). The addition of dppe (3.65 g, 9.2 mmol) in acetone (600 cm^3) gave an initial deep purple solution which became yellow after 12 h.

Ammonium hexafluorophosphate (1.47 g, 9.0 mmol) in water was then added and the solvent was removed under reduced pressure giving a yellow-brown solid. This was collected, washed with water (3 × 50 cm^3), then toluene (3 × 50 cm^3), and the residue was extracted with acetone. An orange-yellow solid (2) (1g) remained unextracted. The filtered extract was concentrated under reduced pressure and addition of water gave yellow crystals of [Mo(η-C$_5$H$_5$)$_2$(dppe)][PF$_6$]$_2$, yield 7g (87%).

Compound (2) could be recrystallised from dichloromethane–methanol, dichloromethane–ethanol, or acetonitrile, yield *ca.* 15%. Its yield increased markedly when the above reaction was carried out at higher temperature (*ca.* 70 °C), yield *ca.* 80%.

Reactions of the Yellow Compound (2).—*With hydrochloric acid.* Compound (2) (200 mg) in CH$_2$Cl$_2$ (20 cm^3) was treated with concentrated HCl (10 cm^3) and the mixture was vigorously shaken for 20 min. Removal of the volatiles gave a yellow solid which was washed with CH$_2$Cl$_2$ and extracted with methanol. Aqueous [NH$_4$][PF$_6$] was added to the extract and the solvent removed under reduced pressure. The residual solid was washed with water and crystallised from acetone–water as yellow *crystals* of [Mo(η-C$_5$H$_5$)$_2$(dppe)][PF$_6$]$_2$, yield *ca.* 60%.

With Na[BH$_4$]. Compound (2) (0.76 g) suspended in dry tetrahydrofuran (30 cm^3) was treated with Na[BH$_4$] (1.5 g). The mixture was stirred at room temperature (r.t.) for 4 h and the solid dissolved giving a bright yellow solution. This was filtered and concentration of the filtrate gave bright yellow microcrystals, yield *ca.* 60%.

With [CPh$_3$][PF$_6$]. Compound (2) (0.5 g) suspended in dry acetonitrile was treated with an excess of [CPh$_3$][PF$_6$] (2.0 g). The suspension rapidly became green and after 1 min water (5 cm^3) was added. The solvent was removed under reduced pressure and the residual oil was washed with toluene (2 × 5 cm^3) and extracted with ethanol. The solvent was removed and the i.r. spectrum of the yellow residue showed it to be [Mo(η-C$_5$H$_5$)$_2$(dppe)][PF$_6$]$_2$.

[1,2-*Bis(diphenylphosphino)ethane*](1—4-η-*cyclopentadiene*)(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate–Dichloromethane* (1/1), (3).—A solution of (1) (0.6 g, 0.66 mmol) in acetone (50 cm^3) was treated with Na[BH$_4$] (30 mg, 0.8 mmol) at room temperature with stirring for 1 h. The resulting yellow solution was taken to dryness under reduced pressure and the residue was extracted with dichloromethane (100 cm^3). Concentration of this solution and further addition of diethyl ether gave yellow crystals of (3), *ca.* 80%. The 1-*exo*-deuterio-analogue (3d) was similarly prepared using Na[BD$_4$] in (CD$_3$)$_2$CO.

[1,2-*Bis(diphenylphosphino)ethane*](η-*cyclopentadienyl*)-(1—3-η-*cyclopentenyl*)*molybdenum* (4).—Compound (3) (160 mg, 0.18 mmol) in freshly distilled thf was treated with 3 cm^3 of a 70% solution of Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] in benzene. After 2 h at room temperature, ethanol (20 cm^3) was carefully added. The solvent was removed and the residue was extracted with dry toluene. Upon concentration and addition of light petroleum, orange crystals of [Mo(η-C$_5$H$_5$)(η^3-C$_5$H$_7$)(dppe)] (4) separated, yield *ca.* 80%.

Alternatively, compound (1) (7 g, 7.66 mmol) suspended in thf (400 cm^3) was treated with Na[BH$_4$] (3 g, 78.9 mmol). The mixture was stirred at r.t. for 2 h and then at 50 °C for another 2 h. The initial solid dissolved giving a dark orange solution. The solvent was removed under reduced pressure, and the residual orange oil was extracted with toluene. This was concentrated and light petroleum (b.p. 100—120 °C) was added. Cooling to *ca.* −40 °C gave orange crystals of [Mo(η-C$_5$H$_5$)(η^3-C$_5$H$_7$)(dppe)], yield *ca.* 60%.

Reaction of [Mo(η-C$_5$H$_5$)(η^4-C$_5$H$_6$)(dppe)][PF$_6$] *with* [CPh$_3$][PF$_6$].—Compound (3) (1 g, 0.12 mmol) in dry dichloromethane (25 cm^3) was treated at r.t. overnight with an excess of [CPh$_3$][BF$_4$]. After 17 h, the resulting yellow precipitate was separated and dissolved in acetone–water (2 : 1). Addition of aqueous [NH$_4$][PF$_6$] gave a yellow precipitate, after partial evaporation of the acetone. This was washed with water (3 × 5 cm^3) and dried. The residue was dissolved in acetone–ethanol (1 : 1) and the solution was concentrated until yellow crystals separated. These were identified from the i.r. spectrum as pure (1), yield *ca.* 50%.

Bis(acetonitrile)bis(η-*cyclopentadienyl*)*molybdenum Bis(hexafluorophosphate)* (17).—The compound [Mo(η-C$_5$H$_5$)$_2$I$_2$] (5.47 g, 11.4 mmol), suspended in acetonitrile (60 cm^3) at 85 °C, was treated dropwise with Tl[PF$_6$] (8.76 g, 25.0 mmol) suspended in acetonitrile (30 cm^3). The mixture was stirred at 85 °C for 12 h. The resulting red solution was filtered from TlI and the filtrate was concentrated. Addition of diethyl ether gave red *crystals* of [Mo(η-C$_5$H$_5$)$_2$(NCMe)$_2$][PF$_6$]$_2$, yield 70%.

[*Bis(diphenylphosphino)methane*]*bis*(η-*cyclopentadienyl*)-*hydridomolybdenum Hexafluorophosphate* (13) *and* [*Bis(diphenylphosphino)methane*]*bis*(η-*cyclopentadienyl*)*molybdenum Bis(hexafluorophosphate)* (12).—The compound [Mo(η-C$_5$H$_5$)$_2$H$_3$][PF$_6$] (5.5 g, 14.7 mmol) in acetone (30 cm^3) was treated with bis(diphenylphosphino)methane (6.21, 16.17 mmol) in acetone (400 cm^3). The purple mixture was left to stand at r.t. for 12 h. Then the resulting yellow solution was treated with [NH$_4$][PF$_6$] (2.6 g, 15.95 mmol) in water (15 cm^3). The solvent was removed and the yellow residue was washed with water (3 × 60 cm^3) and toluene (3 × 50 cm^3) and dried. Extraction with dichloromethane gave a yellow extract and an orange powder. Addition of methanol to the dichloromethane extract gave yellow *crystals* of [Mo(η-C$_5$H$_5$)$_2$(dppm)H][PF$_6$], yield 4.6 g (41%). The orange powder was crystallised from acetone–ethanol (1 : 1) as pale orange crystals of [Mo(η-C$_5$H$_5$)$_2$(dppm)][PF$_6$]$_2$, yield 2.7 g (20%).

[*Bis(diphenylphosphino)methane*]*chlorobis*(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate* (14).—Compound (13) (1.22 g, 3.78 mmol) in dichloromethane (50 cm^3) and chloroform (50 cm^3) was left to stand at room temperature for 15 d. Orange crystals formed (0.1 g) and the initially yellow solution became purple. The solution was filtered and removal of part of the dichloromethane under reduced pressure gave purple crystals. These were washed with methanol and dried, yield 0.7 g (52%). The orange *crystals* were [Mo(η-C$_5$H$_5$)$_2$(dppm)][PF$_6$]$_2$, yield *ca.* 6%.

Reaction of [Mo(η-C$_5$H$_5$)$_2$(NCMe)$_2$][PF$_6$]$_2$ *with* Na[BH$_4$].—The compound [Mo(η-C$_5$H$_5$)$_2$(NCMe)$_2$][PF$_6$]$_2$ (1.6 g, 2.67 mmol) suspended in thf was treated with Na[BH$_4$] (1 g, 26.31 mmol). The mixture was stirred at r.t. for 2 h. The resulting yellow solution was filtered and removal of solvent gave a yellow solid which was extracted with toluene. The toluene extract was concentrated and light petroleum added giving yellow crystals. These were twice recrystallised from toluene–light petroleum at −20 °C, and were identified as [Mo(η-C$_5$H$_5$)$_2$H$_2$] from the i.r. and ^{1}H n.m.r. spectra, yield *ca.* 70%.

[1,2-*Bis(diphenylphosphino)ethane*]*trichloro*(η-*cyclopentadienyl*)*molybdenum–methanol* (1/1), (5).—Compound (4) in toluene (500 cm^3) at −40 °C was treated with hydrogen chloride gas for 8 min. A red oily precipitate separated. The solvent was removed and the red residue was extracted with the minimum quantity of dichloromethane. The extract was filtered into methanol saturated with hydrogen chloride (30 cm^3). Red crystals formed after 12 h. The crystals were washed with methanol and dried, yield 7.4 g (49%). The volatile products evolved in this reaction were studied by g.l.c. on a 10% KCl–alumina column and shown to include cyclopentene.

[1,2-*Bis(diphenylphosphino)ethane*](*η-cyclopentadienyl*)-*trihydridomolybdenum* (6).—Compound (5) (3 g, 4.5 mmol) in toluene (60 cm^3) was treated with a 70% solution of Na-[$AlH_2(OCH_2CH_2OMe)_2$] in benzene (3 g, 14.9 mmol). After 12 h at r.t. the red solid had reacted, giving a yellow solution. This was cooled to *ca.* −10 °C and ethanol added dropwise with vigorous shaking until hydrogen evolution ceased. The solvent was removed under reduced pressure and the resulting yellow oil was extracted with the minimum amount of toluene and chromatographed on an alumina column made up in light petroleum (b.p. 60—80 °C). Elution with toluene gave a yellow band. The eluate was concentrated and light petroleum (b.p. 100—120 °C) was added. Cooling to −40 °C gave yellow crystals, yield *ca.* 50%.

Reaction of [$Mo(\eta-C_5H_5)(dppe)Cl_3$] *with* Na[$BH_4$].—The compound [$Mo(\eta-C_5H_5)(dppe)Cl_3$] (2 g, 3.0 mmol) in dry thf (100 cm^3) was treated with Na[BH_4] (3 g, 79.3 mmol) at r.t. for *ca.* 2 h giving a green solution. The solvent was removed and the green oily residue was extracted with light petroleum. The green petroleum solution was concentrated under vacuum, and cooled to 0 °C, giving a green powder, yield *ca.* 25%.

[1,2-*Bis(diphenylphosphino)ethane*](*η-cyclopentadienyl*)-(1—3-*η-1-methylallyl*)*molybdenum* (7).—Compound (6) (0.2 g, 0.36 mmol) in toluene (5 cm^3) and butadiene (2 cm^3) were sealed in an ampoule. The mixture was heated at 70 °C for 12 h giving orange crystals. These were crystallised from light petroleum (b.p. 60—80 °C) at −20 °C, yield *ca.* 70%. Comparison of the i.r. and ^1H n.m.r. spectra with those of an authentic sample [5] showed the *compound* to be [$Mo(\eta-C_5H_5)(\eta^3-1Me-C_3H_4)(dppe)$].

[1,2-*Bis(diphenylphosphino)ethane*](1—4-*η-butadiene*)(*η-cyclopentadienyl*)*molybdenum Hexafluorophosphate* (8).—Compound (7) (0.1 g, 0.16 mmol) in dry dichloromethane (20 cm^3) was treated with [CPh_3][PF_6] (0.065 g, 0.17 mmol) in dry dichloromethane (20 cm^3) and the mixture was heated at 50 °C for 1 h. Then dry diethyl ether was added and a yellow solid precipitated. This was washed with ethanol and the orange residue was crystallised from acetone–ethanol as orange *crystals* of [$Mo(\eta-C_5H_5)(\eta-C_4H_6)(dppe)$]-[$PF_6$], yield *ca.* 70%.

[1,2-*Bis(diphenylphosphino)ethane*](*η-cyclopentadienyl*)-*dihydrido(tri-n-butylstannio)molybdenum* (10).—Compound (5) (0.6 g, 0.9 mmol) was suspended in dry toluene (50 cm^3) and treated with $SnBu^n{}_3H$ (0.84 g, 2.9 mmol). The mixture was heated at 110 °C for *ca.* 30 min. After removal of solvent the residual oil was chromatographed on an alumina column made up in light petroleum (b.p. 60—80 °C). After elution with toluene–diethyl ether the product was crystallised from toluene–light petroleum at −40 °C as yellow crystals, yield *ca.* 50%.

Reaction of [$Mo(\eta-C_5H_5)(dppe)H_3$] *with* $CHBr_3$.—The compound [$Mo(\eta-C_5H_5)(dppe)H_3$] (0.5 g, 0.89 mmol) in toluene (30 cm^3) was treated with an excess of $CHBr_3$. The solution, initially yellow, became red. The solution was concentrated by warming, under reduced pressure, and allowed to cool to room temperature, giving some red crystals. These were collected, washed with light petroleum, and dried under vacuum, yield *ca.* 70%. The red crystals could be recrystallised from dichloromethane–methanol.

[*Bis(diphenylphosphino)methane*](*η-cyclopentadienyl*)(*η-cyclopentenyl*)*molybdenum* (15).—Compound (12) (1 g, 1.1 mmol) suspended in dry thf (50 cm^3) was treated with Na[BH_4] (0.3 g, 7.8 mmol) at r.t. for 30 min. The solvent was removed and the residual orange oil was extracted with toluene. The extract was concentrated, light petroleum (b.p. 100—120 °C) was added, and the solution was cooled at −40 °C for 48 h. Orange crystals and colourless needles were formed. These were washed with acetone, when the colourless needles dissolved. The orange crystals were dried *in vacuo*, yield *ca.* 40%.

[*Bis(diphenylphosphino)methane*]*trichloro*(*η-cyclopentadienyl*)*molybdenum*. (16).—Compound (12) (0.8 g, 0.89 mmol) suspended in dry thf (50 cm^3) was treated with Na[BH_4] as described above. The orange residue in toluene was treated with hydrogen chloride giving a red oil. This was crystallised from dichloromethane–methanol (1 : 1) as purple *crystals* of [$Mo(\eta-C_5H_5)(dppm)Cl_3$], yield *ca.* 50%.

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