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NUCLEOPHILIC ATTACK ON BENT MOLYBDENUM AND TUNGSTEN METALLOCENE COMPLEXES

ALBERTO R. DIAS and CARLOS C. ROMÃO
Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)

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Summary

Reactions of some $[M(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$ complexes (M = Mo, W; L = ligand; $n = 0, 1, 2$) with $NaBH_4$ and $LiAlH_4$ are reported. New neutral and cationic hydride derivatives of the type $[M(\eta^5\text{-}C_5H_5)_2HL]^{m+}$ ($m = 0, 1$) are described, in particular the six halohydride complexes $[M(\eta^5\text{-}C_5H_5)_2HX]$. The deuteration studies were carried out, but the results do not lead to definite conclusions about the mechanism.

Introduction

As Green has pointed out [1], the vast majority of the reactions undergone by molybdenum and tungsten complexes of the type $[M(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$ do not involve the $M(\eta^5\text{-}C_5H_5)_2$ moiety, and this fragment is remarkably stable. However, it has been shown that, in the case of nucleophilic attack of hydride ion on $[Mo(\eta^5\text{-}C_5H_5)_2(dppe)]^{2+}$, the reaction center is one of the $\eta^5\text{-}C_5H_5$ rings [2]. Similarly, $(C_6F_5)^-$ adds to one of the rings of $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Mo, W) to give $[M(\eta^5\text{-}C_5H_5)(C_5H_4C_6H_5)H(C_6H_5)]$ [3], and the reaction of $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ with $LiAlD_4$ leads to a partially ring-deuterated product [4]. Furthermore, reaction of $[Mo(\eta^5\text{-}C_5H_5)_2Cl(Et)]$ with trialkylphosphines gives $[Mo(\eta^5\text{-}C_5H_5)(endo\text{-}\eta^4\text{-}C_5H_4Et)Cl(PR_3)]$ involving metal-to-ring migration of the ethyl group [5]. Another example of this type of reaction has been reported for $[V(\eta^5\text{-}C_5H_5)_2Ph]$ [6].

These results suggest that a closer look at reactions in which the cyclopentadienyl rings may be involved will be fruitful, and we describe below some studies of the nucleophilic substitution reactions of hydride with some $M^{IV}(\eta^5\text{-}C_5H_5)_2$ (M = Mo, W) derivatives.

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TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analysis (found (calcd.) (%))			^{1}H NMR [a] τ, multiplicity, relative area assignment	IR [b] ν(M—H) (cm^{-1})
		C	H	N		
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]}$ (II)	purple-blue	36.6 (36.7)	3.5 (3.6)		2.2, m, 5, $\mathrm{C_6}H_5$; 4.2, d(J(^{31}P—M) 2 Hz), 10, $\mathrm{C_5}H_5$; 7.79, d(J(^{31}P—H) 10 Hz), 6, $\mathrm{C}H_3$	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2Cl(NH_3)][PF_6]}$ (III)	dark green	28.7) (28.4)	3.6 (3.1)	3.5 (3.3)	4.08, s, 10, $\mathrm{C_5}H_5$; 6.87, broad, 3, $\mathrm{N}H_3$	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2Br(NH_3)][PF_6]}$ (IV)	dark green	26.1 (25.6)	3.2 (2.8)	3.2 (3.0)	4.37, s, 10, $\mathrm{C_5}H5$; 6.88, broad, 3, $\mathrm{N}H_3$	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2(SCH_2CH_2SMe)]I}$ (VI) [c]	orange	33.5 (33.9)	3.7 (3.7)		[d] 4.36, s, 10, $\mathrm{C_5}H_5$; 7.15, t, 2, $\mathrm{C}H_2$; 7.33, s, 3, $\mathrm{C}H_3$; 7.82, t, 2, $\mathrm{C}H_2$	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2H(PMe_2Ph)][PF_6]}$ (VIII)	yellow	[e]			2.44, m, 5, $\mathrm{C_6}H_5$; 4.93, d (J^{31}P—H) 2.9 Hz), 10, $\mathrm{C_5}H_5$ 8.2, d (J(^{31}P—H) 10 Hz), 6, $\mathrm{CH_3}$; 18.93d (J(^{31}P—H) 36 Hz) 1, Mo-H	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2H(SCH_2CH_2SMe)]}$ (IX)	orange	46.7 (46.7)	5.3 (5.4)		4.99, s, 10, $\mathrm{C_5H_5}$; 7.62, m [f], 4, $\mathrm{C}H_2$; 7.9, s [g], $\mathrm{C}H_3$; 17, 77, s, Mo-H	
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2HCl]}$ (X)	brown-red	45.8 (45.7)	4.6 (4.2)		4.95, s, 10, $\mathrm{C_5}H_5$; 18.90, s, 1, Mo-H	1848
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2HBr]}$ (XI)	brown	39.3 (39.1)	3.6 (3.6)		4.89, s, 10, $\mathrm{C_5}H_5$; 19.13, s, 1, Mo-H	1873
$\mathrm{[Mo(\eta\text{-}C_5H_5)_2HI]}$ (XII)	green	[h]			4.87, s, 10, $\mathrm{C_5}H_5$; 19.20, s, 1, Mo-H	1860
$\mathrm{[W(\eta\text{-}C_5H_5)_2HCl]}$ (XIII)	brown-red	[i]			5.08, s, 10, $\mathrm{C_5}H_5$; 22.17, t (J(^{183}W—H) 62 Hz), 1, W-H	1968
$\mathrm{[W(\eta\text{-}C_5H_5)_2HBr]}$ (XIV)	brown	30.9 (31.1)	3.1 (3.9)		4.98, s, $\mathrm{C_5}H_5$; 22.55, t (J(^{183}W—H) 62 Hz), 1, W-H	1955
$\mathrm{[W(\eta\text{-}C_5H_5)_2HI]}$ (XV)	green	27.6 (27.2)	2.7 (2.5)		4.98, s, 10, $\mathrm{C_5}H_5$; 22.97, t (J(^{183}W—H) 62 Hz), 1, W-H	1935
$\mathrm{[W(\eta\text{-}C_5H_5)_2H(SCH_3)]}$ (XVI)	orange	35.9 (36.5)	4.0 (3.9)		4.90, s, 10, $\mathrm{C_5}H_5$; 8.18, s, 3, $\mathrm{C}H_3$; 21.28, t (J(^{183}W—H) 75 Hz, 1, W-H	1900
$\mathrm{[W(\eta\text{-}C_5H_5)_2H(SPh)]}$ (XVII)	yellow-orange	45.6 (45.3)	4.0 (3.8)		2.9, m, 5, $\mathrm{C_6}H_5$; 5.03, s, 10, $\mathrm{C_5}H_5$; 21.38, t (J(^{183}W—H) 71 Hz), 1, W-H	1925

[a] In $\mathrm{Me_2CO}$-d_6, τ relative to external TMS; s, singlet; d, doublet; t, triplet; m, multiplet. [b] As Nujol mulls. [c] Λ_M (Ω^{-1} cm^2 mol^{-1}) 88 in 10^{-3} M solution in $\mathrm{NO_2Me}$. [d] In DMSO-d_6. [e] Identified in solution by ^{1}H NMR compared with $\mathrm{[Mo(\eta\text{-}C_5H_5)_2H(PMe_2Ph)]I}$. [f] Symmetric 16 lines. [g] Superimposed on other lines. [h] Described in [11]. [i] Described in [12].

Chemical studies

Reaction of $[M(\eta^5\text{-}C_5H_5)_2X_2]$ (I): M = Mo, W; X = Cl, Br, I) with a ligand L, in the presence of 1 or 2 molar equivalents of $Tl[PF_6]$, in refluxing acetone, acetonitrile, or dimethyl sulfoxide is a well established method [7] for the preparation of cationic complexes of the type $[M(\eta^5\text{-}C_5H_5)_2XL]^+$ and $[M(\eta^5\text{-}C_5H_5)_2L_2]^{2+}$. The new complexes: $[Mo(\eta^5\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$ (II), $[Mo(\eta^5\text{-}C_5H_5)_2Cl(NH_3)][PF_6]$ (III) and $[Mo(\eta^5\text{-}C_5H_5)_2Br(NH_3)][PF_6]$ (IV), as well as the known complex $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)_2][PF_6]_2$ (V) [8], were prepared in this way. The new complex $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SMe)][PF_6]$ (VI) was prepared by methylation of $[Mo(\eta^5\text{-}C_5H_5)_2\{S_2(CH_2)_2\}]$ with MeI, as was described for the tungsten analogue [9]. Relevant data for the characterization of these complexes, and all other new complexes prepared in the course of this work are presented in Table 1.

Treatment of tetrahydrofuran (THF) suspensions of III, IV, V and of complex $[Mo(\eta^5\text{-}C_5H_5)_2(acac)]^+$ (VII) [10] with $NaBH_4$ at room temperature gave the dihydride $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in quantitative yield. On the other hand, under the same conditions, monocations II and VI yielded the mono-hydrido complexes $[Mo(\eta^5\text{-}C_5H_5)_2H(PMe_2Ph][PF_6]$ (VIII) and $[Mo(\eta^5\text{-}C_5H_5)_2H(SCH_2CH_2SMe)]$ (IX), respectively.

Treatment of the dihalide complexes I, suspended in THF containing about 3% (v/v) of water, with $NaBH_4$ at ~50°C gave brown solutions after 4 h reaction. Work-up of these solutions conveniently affords two complexes in varying relative yield: the dihydride $[M(\eta^5\text{-}C_5H_5)_2H_2]$ and the corresponding halohydride $[M(\eta^5\text{-}C_5H_5)_2HX]$. Under comparable reaction conditions the molybdenum dihalides give a greater proportion of dihydride than do their tungsten analoges. Use of longer reaction times, higher temperatures, or $LiAlH_4$ as reductant yields only the dihydride in both the molybdenum and tungsten series.

By careful control of the reaction conditions and work-up, we were able to isolate the complete set of six halohydride complexes $[M(\eta^5\text{-}C_5H_5)_2HX]$ (M = Mo, W; X = Cl, Br, I); only two of these (M = Mo, X = I; M = W, X = Cl) were previously known, and had been prepared by different routes [11,12]. A noteworthy observation is that in these halohydride complexes the ^1H NMR chemical shift of the hydride shows a regular dependence on the electronegativity of X, whereas no trend is observable for the cyclopentadienyl proton resonance.

The related bis-thiolato complexes $[W(\eta^5\text{-}C_5H_5)_2(SR)_2]$ [13] do not react with $NaBH_4$ under these conditions, but they do react with $LiAlH_4$, giving the mono-thiolato complexes $[W(\eta^5\text{-}C_5H_5)_2H(SR)]$ (R = Me, Ph).

Labelling experiments

In order to probe the possible involvement of the cyclopentadienyl ring in the reactions described above, several of them were repeated using $NaBD_4$ or $LiAlD_4$ in rigorously dried solvents; these reactions are summarised in Table 2.

Since our main interest was in determining the presence or absence of C—D bonds in the $\eta^5\text{-}C_5H_5$ rings, several of the resulting hydride (deuteride) species were not isolated as such but instead were treated with halocarbons which introduce halide in place of a hydride ligand. The resulting halides are more stable

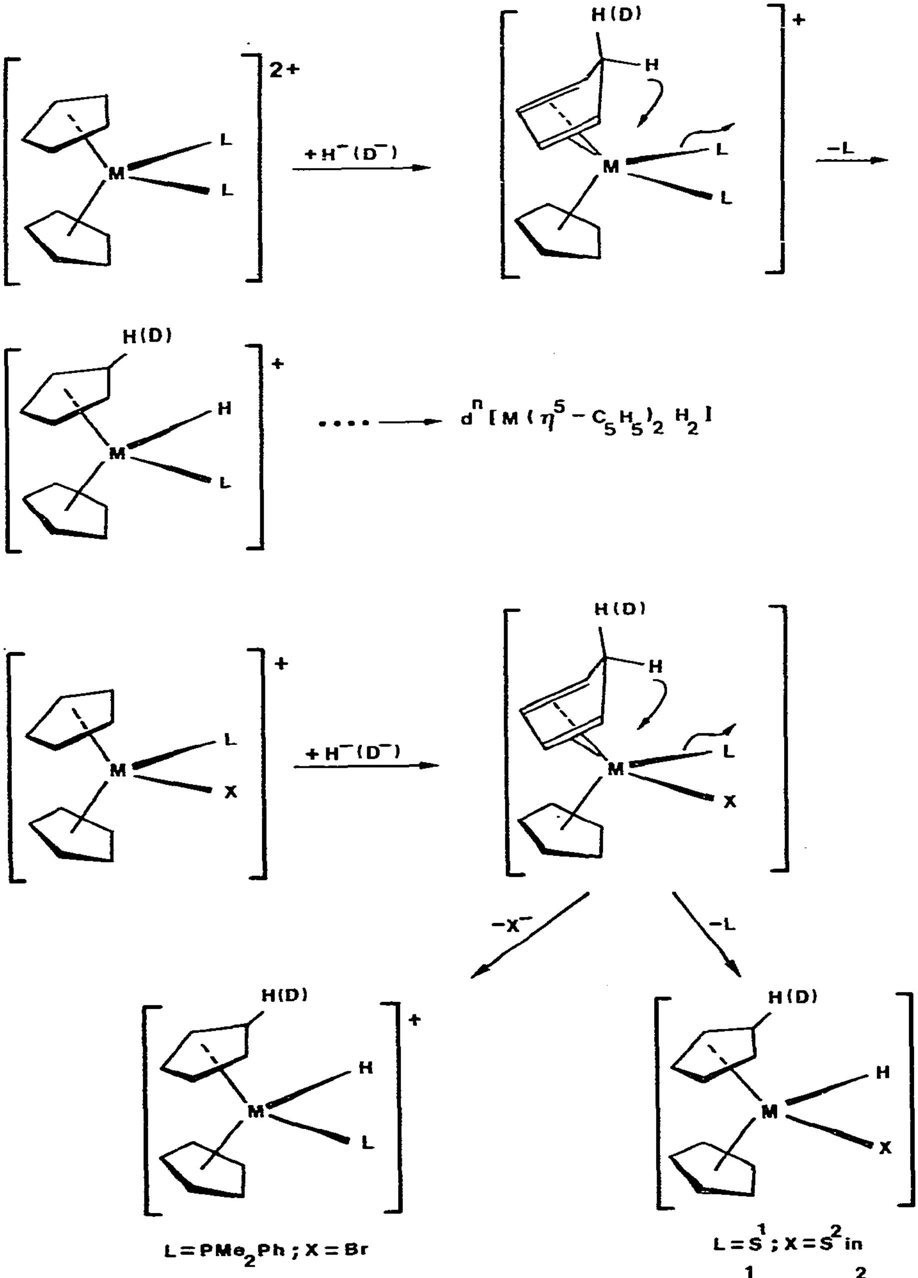
TABLE 2

LABELLING EXPERIMENTS

Experiment	Reactants	Conditions	Products isolated	Isolation method [a]	Selected IR data (cm^{-1})
D1	$[Mo(\eta\text{-}C_5H_5)_2Cl_2] + LiAlD_4$	THF, 50°C	$d^n[Mo(\eta\text{-}C_5H_5)_2H_2]$	*a*	2305vw(C-D); 1840s(Mo-H); 1330m(Mo-D)
D2	$[W(\eta\text{-}C_5H_5)_2Cl_2] + LiAlD_4$	THF, 50°C	$d^n[W(\eta\text{-}C_5H_5)_2H_2]$	*a*	2301w(C-D); 1930s(W-H); 1360(W-D)
D3	$[Mo(\eta\text{-}C_5H_5)_2(SPh)_2] + LiAlD_4$	THF, 50°C	$d^n[Mo(\eta\text{-}C_5H_5)_2Cl_2]$	*b*	2310w(C-D)
D4	$[W(\eta\text{-}C_5H_5)_2Cl_2] + NaBD_4$	THF; reflux; 48 h	$d^n[W(\eta\text{-}C_5H_5)_2HCl]$	*c*	2320w(C-D); 1930s(W-H); 1360m(W-D)
D5	$[Mo(\eta\text{-}C_5H_5)_2HBr] + NaBD_4$	1,2-DME; reflux	$d^n[Mo(\eta\text{-}C_5H_5)_2Cl_2]$	*b*	as in D3
D6	$[Mo(\eta\text{-}C_5H_5)_2I_2] + NaBD_4$	1,2-DME; reflux; 2,5 h	$d^n[Mo(\eta\text{-}C_5H_5)_2H_2]$	*d*	identical to D1 for d^n-$[Mo(\eta\text{-}C_5H_5)_2H_2]$
			$d^n[Mo(\eta\text{-}C_5H_5)HI]$		2315vw(C-D); 1863m(Mo—H) for $d^n[Mo(\eta\text{-}C_5H_5)_2HI]$
D7	$[Mo(\eta\text{-}C_5H_5)_2H_2] + NaBD_4$	1,2-DME; reflux; 2,5 h	$[Mo(\eta\text{-}C_5H_5)_2H_xD_{2-x}]$	*c*	1840s(Mo-H); 1330m(Mo-D)
D8	$[Mo(\eta\text{-}C_5H_5)_2H_2] + D_2O$	*a*	$[Mo(\eta\text{-}C_5H_5)_2H_xD_{2-x}]$	*c*	1845w(Mo-H); 1333s(Mo-D)
D9	$[Mo(\eta\text{-}C_5H_5)_2(NH_3)_2][PF_6]_2$	1,2-DME; 50°C; 6 h	$d^n[Mo(\eta\text{-}C_5H_5)_2H_2]$	*a*	identical to D1
D10	$[Mo(\eta\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$ + $NaBD_4$	$Me_2CO\text{-}d_6$	$d^n[Mo(\eta\text{-}C_5H_5)_2Br]$ $[(PMe_2Ph)][PF_6]$	*f*	2320w(C-D)

[a] See experimental section.

and easier to purify. By "d^n dihydride" in Table 2, we mean a species whose properties (color, air stability, ease of sublimation, and solubility) are identical with those of $[M(\eta^5\text{-}C_5H_5)_2H_2]$ except for the IR spectrum, where both C—H and C—D as well as M—D and M—H stretching bands are present; thus, n is the total number of D atoms in "d^n dihydride" (not determined) irrespective of the actual position of deuterium (at the ring and/or at the metal) in the complex.

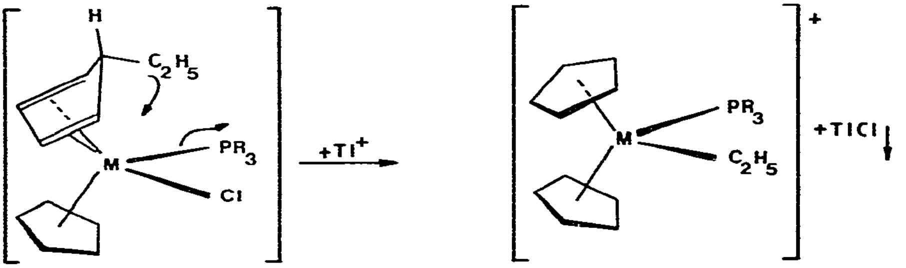


SCHEME 1

Discussion

The products obtained from the reaction of $[MCp_2L_2]^{1+,2+}$ derivatives with $NaBH_4$ or $LiAlH_4$ are either $[MCp_2H_2]$ or $[MCp_2HL]^{0,1+}$. Although these results are in contrast to the behaviour of the dication $[MoCp_2dppe]^{2+}$ where H^- attacks at the *exo*-face of one of the η^5-C_5H_5 rings to give the cyclopentadiene complex $[Mo(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)dppe]^+$ [2] we believe that an analogous mechanism operates i.e. an initial attack of H^- (D^-) at a η^5-C_5H_5 ring is followed by migration of *endo*-H in an intermediate η^4-C_5H_6-η^4-C_5H_5D complex to give the final product, as shown in Scheme 1.

Such a mechanism is in agreement with some recent generalizations about the regioselectivity of nucleophilic additions to organometallic cations containing unsaturated hydrocarbons. The difference in the products obtained may be ascribed to thermodynamic rather than kinetic control in the case of cations II—VI. A similar *endo* migration, but of ethyl rather than hydride, was observed by Benfield and Green [5] (Scheme 2).



SCHEME 2

For neutral complexes the data available do not allow a definitive mechanistic assignment. The possibility of direct attack on the metal followed by D^-/H^- migration to the ring is excluded since the results of labelling experiments D8, ($[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ + D_2O/THF) and D7 ($[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ + $NaBD_4$), show that no intra- or intermolecular metal-to-ring H/D exchange takes place in $[Mo(\eta^5\text{-}C_5H_5)_2H_xD_{2-x}]$, since only partial deuteration at the metal was observed in both experiments. Experiment D7 is consistent with a report by Cooper and Green that no ring deuteration occurs in the reaction of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ with $LiAlD_4$ [4].

The possibility that ring deuteration occurs by means of intramolecular H/D exchange in species such as $[M(\eta^5\text{-}C_5H_5)_2(BD_4)]^+$ [15] cannot be entirely ruled out by our results, but no evidence for such an intermediate was detected and the covalency of Mo—H and W—H bonds certainly argues against the stability of such species [16,17]. Finally either a mechanism analogous to that proposed for the cationic complexes or an intermolecular mechanism are not excluded by the data now available. A more detailed analysis by mass spectrometry of the products from deuteration studies is now under way.

Experimental

All preparations were carried out under dry N_2. Solvents were dried and distilled over sodium benzophenone ketyl immediately before use. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) used in the labelling experiments were dried in the same way, then refluxed over $LiAlH_4$ and finally distilled under vacuum directly into the reaction vessel. The IR spectra were determined on a Perkin—Elmer 457 spectrophotometer as KBr pellets and the ^1H NMR spectra recorded on a JEOL JNM-100-PFT spectrometer. Microanalyses were performed in our laboratory, or by A.G. and G.F. Olney, Ditchling, Hassocks, England.

The parent dihydrides $[M(\eta^5\text{-}C_5H_5)_2H_2]$ (M = Mo, W) were prepared by the procedure used by Green and Knowles [18]. The dihalide derivatives $[M(\eta^5\text{-}C_5H_5)_2X_2]$ (M = Mo, W; X = halide) were prepared as described by Cooper and Green [4].

Preparation of $[Mo(\eta^5\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$. A suspension of $[Mo(\eta^5\text{-}C_5H_5)_2Br_2]$ (0.45 g; 1.04 mmol) and Tl $[PF_6]$ (0.37 g; 1.06 mol) in acetone (30 cm^3) was treated with excess (0.2 cm^3) PMe_2Ph and heated at reflux for 2 h. After filtration to separate TlBr, the purple solution was taken to dryness in vacuum and the residue washed with Et_2O (5 X 5 cm^3). A first recrystallization from acetone/toluene, followed by a recrystallization from acetone/Et_2O gave purple crystals (85%) of $[Mo(\eta^5\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$.

Preparation of $[Mo(\eta^5\text{-}C_5H_5)_2X(NH_3)][PF_6]$ *and* $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)_2][PF_6]_2$ *(X = Cl, Br).* A solution of $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ (1.0 g; 3.4 mmol) and $Tl[PF_6]$ (1.2 g; 3.4 mmol) in DMSO (30 cm^3) was treated with gaseous NH_3 for 15 minutes. The purple mixture was evaporated at reduced pressure (~95°C) and the resulting oil washed with toluene (5 X 10 cm^3), Et_2O (5 X 10 cm^3) and CH_2Cl_2 (3 X 5 cm^3) and then dried in vacuum. Extraction with acetone gave a greenish solution which was taken to dryness in vacuum. Extraction of this residue with MeOH followed by concentration gave dark green crystals of $[Mo(\eta^5\text{-}C_5H_5)_2Cl(NH_3)][PF_6]$; yield ca. 40%. Starting with $[Mo(\eta^5\text{-}C_5H_5)_2Br_2]$ and using MeCN as solvent, $[Mo(\eta^5\text{-}C_5H_5)_2Br(NH_3)][PF_6]$ was obtained in 70% yield. When the reaction was carried out under similar conditions but with a 1/2 (Mo/Tl) molar ratio the compound $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)_2][PF_6]_2$ was isolated in 60% yield.

Preparation of $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SCH_3)]$ *I.* CH_3I (2 cm^3) was added to a saturated solution of $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2S)]$ (0.55 g; 1.7 mmol) in CH_2Cl_2. After 30 minutes orange crystals separated and were filtered off, washed with Et_2O (2 X 5 cm^3) and dried. Yield of $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SCH_3)]I$, 95%.

Reactions of $[Mo(\eta^5\text{-}C_5H_5)_2(acac)][BF_4]$, $[Mo(\eta^5\text{-}C_5H_5)_2X(NH_3)][PF_6]$ *(X = Cl, Br) and* $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)_2][PF_6]_2$ *with* $NaBH_4$. Essentially the same procedure was employed for all these reactions: a suspension of 0.5 mmol of the cation in THF was treated with excess $NaBH_4$ (2 mmol) at room temperature with stirring until all the complex dissolved. The mixture was taken to dryness and extracted with dry toluene. Upon concentration and cooling of the extract, crystals of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ were obtained in essentially quantitative yield.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SCH_3)]$ I *with* $NaBH_4$. A suspension of $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SCH_3)]$ I in dry THF (30 cm^3) was treated with excess $NaBH_4$ at room temperature. No reaction was apparent after 1.5 h, but one started upon addition of 5 drops of water. After 2 h the orange solution was taken to dryness. The toluene extract of the residue was concentrated and cooled to ~ −20°C, yielding $[Mo(\eta^5\text{-}C_5H_5)_2(SCH_2CH_2SCH_3)(H)]$ as orange crystals (80%).

Reaction of [Mo(η^5-C_5H_5)$_2$Br(PMe_2Ph)][PF_6] with $NaBH_4$. A solution of [Mo(η^5-C_5H_5)$_2$Br(PMe_2Ph)][PF_6] (0.5 mmol) in acetone (25 cm^3) was treated with excess $NaBH_4$ (3 mmol) at room temperature for 1.5 h. The yellow solution was taken to dryness and the residue was washed with toluene (5 × 5 cm^3) and then Et_2O (5 × 5 cm^3). The residue was chromatographed on acid alumina (column prepared in light petroleum). After elution with toluene (200 cm^3) to remove residual phosphine, elution with acetone gave a yellow band from which a yellow powder was recovered. This could not be properly recrystallized but was identified as [Mo(η^5-C_5H_5)$_2$H(PMe_2Ph)][PF_6] from the ^{1}H NMR spectrum in M_2CO-d_6 (which was identical to that observed for [Mo(η^5-C_5H_5)$_2$H(PMe_2Ph)] I [19]) and by isolation of [Mo(η^5-C_5H_5)$_2$Br(PMe_2Ph)][PF_6] when $CHBr_3$ was added to an acetone solution of the yellow residue.

Reaction of [M(η^5-C_5H_5)$_2X_2$] with $NaBH_4$ (M = Mo, W; X = Cl, Br, I, SR); The following procedure is a typical preparation and was used with minor variations for the entire series. A suspension of 1 mmol of [M(η^5-C_5H_5)$_2X_2$] in THF (30 cm^3) and 1 cm^3 of water, was treated with a large excess of $NaBH_4$ (6 mmol) at 50°C. After 4 h, or when no more dihalide remained in suspension, the solvent was evaporated and the residue extracted with warm toluene. Upon concentration of the brown solutions, crystals of the halohydrides [M(η-C_5H_5)$_2$-HX] separated. (Alternatively, 1,2-dimethoxyethane can be used as solvent; in this case added water is not required in order to initiate reaction.) For reactions with M = Mo some [Mo(η^5-C_5H_5)$_2H_2$] is always formed. In these cases the toluene extract was chromatographed on an alumina column prepared in light petroleum, elution with toluene afforded the dihydride and a elution with CH_2Cl_2/acetone (1/1) gave the halohydride. The eluates, in all cases, were recrystallized from toluene. When reactions were allowed to continue for more than 16 h, [M(η^5-C_5H_5)$_2H_2$] was formed in almost quantitative yield from all the dihalide complexes. In rigorously dry THF these reactions are very slow.

No reaction of [Mo(η^5-C_5H_5)$_2$($S_2H_2CH_2S$)] or [W(η^5-C_5H_5)$_2$(SR)$_2$] (R = Me, Ph) with $NaBH_4$ was observed under these conditions.

Reactions of [W(η^5-C_5H_5)$_2$(SR)$_2$] (R = Me, Ph) with $LiAlH_4$. A suspension of 0.5 mmol of [W(η^5-C_5H_5)$_2$(SPh)$_2$] in dry THF (20 cm^3) was treated at room temperature with $LiAlH_4$ (1 mmol) until all the starting complex dissolved (30 min). The mixture was then evaporated at a temperature below 25°C, and cold ethanol was added until no further reaction was observed. The mixture was then taken to dryness and the residue extracted with toluene. Upon evaporation and addition of pentane to the extract, yellow-orange crystals of [W(η^5-C_5H_5)$_2$H(SPh)] separated in 60% yield.

A similar procedure was followed for the preparation of [W(η^5-C_5H_5)$_2$H(SMe)] from [W(η^5-C_5H_5)$_2$(SMe)$_2$], but 1,2-dimethoxyethane was used as solvent, since reaction in THF was very slow. The yield was 40%.

Labelling experiments (Table 2)

Some typical experiments, chosen to illustrate the isolation methods, are described.

Isolation method (a). A suspension of [Mo(η^5-C_5H_5)$_2H_2$] in rigorously dried THF was treated with a two-fold excess of $LiAlD_4$ at 50°C until the solution turned light yellow. The solvent was evaporated under vacuum and the residue extracted with dry toluene. The yellow solution was pumped to dryness and the residue sublimed on to a cold finger inserted into the reaction vessel.

Isolation method (b). $[Mo(\eta^5\text{-}C_5H_5)_2(SPh)_2]$ was treated with $LiAlD_4$ as described above for the dihydride. The yellow solution obtained was taken to dryness, the residue was extracted with dry toluene, and 5 cm^3 of CCl_4 was added to the extract. Green crystals quickly precipitated, and were washed with dry toluene and with dry diethyl ether, and then dried under vacuum.

Isolation method (c). The reaction of $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ with a five-fold excess of $NaBD_4$ in refluxing THF took place very slowly. After two days, with unchanged dichloride still present, the solvent was evaporated. The residue was extracted with dry toluene and the brown solution concentrated under vacuum until deep red crystals separated. These were filtered off, washed with dry diethyl ether and dried under vacuum.

Isolation method (d). The reaction of $[Mo(\eta^5\text{-}C_5H_5)_2I_2]$ with $NaBD_4$ was performed as in the examples above but in refluxing 1,2-dimethoxyethane for 2.5 h. After evaporation of the solvent the residue was extracted with dry toluene. Upon concentration, green crystals of $d^n[Mo(\eta^5\text{-}C_5H_5)_2HI]$ separated, and these were washed with pentane. The mother liquor was filtered, taken to dryness, and "$d^n[Mo(\eta\text{-}C_5H_5)_2H_2]$" recovered by sublimation as in (*a*).

Isolation method (e). A solution of freshly sublimed $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ (150 mg) in a mixture of dry THF (15 cm^3) and 1 cm^3 of D_2O was heated at reflux for 2 h and then taken to dryness. The same treatment was repeated twice more, and the resulting residue, $[Mo(\eta\text{-}C_5H_5)_2H_xD_{2-x}]$ was thoroughly dried under vacuum.

Isolation method (f). A solution of $[Mo(\eta^5\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$ (200 mg) in $Me_2CO\text{-}d_6$ (10 cm^3) was treated with a two-fold excess of $NaBD_4$. When the solution became yellow, the solvent was evaporated and the residue extracted with CH_2Cl_2. $CHBr_3$ (2 cm^3) was added to the yellow extract, causing a rapid color change to deep purple. The purple product was recrystallized from CH_2Cl_2/Et_2O to give needles of $d^n[Mo(\eta^5\text{-}C_5H_5)_2Br(PMe_2Ph)][PF_6]$.

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