ORGANOMETALLICS

Hydride Abstraction from [MCp^{Bz}(CO)₃H] (M = Mo, W; Cp^{Bz} = $C_5(CH_2Ph)_5$): New Cationic Complexes Stabilized by $\eta^5:\eta^2-C_5H_4:C_6H_5$ Bonding of the Pentabenzylcyclopentadienyl Ligand

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Supporting Information

ABSTRACT: Hydride abstraction from $[MCp^{Bz}(CO)_3H]$ (M = Mo, W; $Cp^{Bz} = C_3(CH_2Ph)_5)$ using trityl cations led to $[M\{\eta^{5:}\eta^2-C_5Bz_4CH_2Ph\}(CO)_3]BAr_F$ (BAr_F = B(3,5-C₆H₃(CF₃)₂)₄; M = Mo (3), W (4)) or $[MCp^{Bz}(CO)_3(FBF_3)]$ (M = Mo (5), W (6)) depending on the trityl counterions. The stabilization of the acidic metal centers in 3 and 4 is made through the coordination of a C==C bond of one phenyl ring, generating ansa-bridged cyclopentadienyl-phenyl carbonyl complexes. 5 and 6 are zwitterionic compounds stabilized by the coordination of the BF₄ anion. An exchange process between coordinated and noncoordinated phenyl rings occurs in dichloromethane solutions of 3. VT NMR experiments gave the exchange rate at various temperatures and $\Delta G^{\ddagger}_{298} = 10.1 \pm 0.2$ kcal mol⁻¹. In 4 the phenyl bonding is static at room temperature, on the NMR time scale. Reactions of 3 and 4 with CO and H₂O led to $[MCp^{Bz}(CO)_4]BAr_F$ (M = Mo (7), W (8)) and $[MCp^{Bz}(CO)_3(OH_2)]BAr_F$ (M = Mo (11), W (12)). In CH₂Cl₂ solutions 3 and 4 convert slowly to 7 and 8, respectively. DFT calculations attest to the stability of 3 to H₂O bonding and also show that the replacement of phenyl coordination by CO is a favorable process ($\Delta H = -13.8$ kcal mol⁻¹).



INTRODUCTION

Hemilabile ligands display important roles in the stabilization and reactivity of metal complexes with significant implications in catalysis. Classic examples for this behavior are allylic η^3/η^1 and indenyl η^5/η^3 shifts,^{1,2} but the array of ligands displaying hemilabile behavior and their participation in a increasing number of catalytic processes have grown extraordinarily with the emergence of chelating polyfunctional ligands that may readily tune and support complex reactivity by changing their bonding modes.³ The good kinetic and thermodynamic properties provided by the cyclopentadienyl ring to organometallic complexes encouraged its use as a basic frame for the building of chelating polyfunctional ligands in combination with soft or hard donors.⁴ However, the connection of cyclopentadienyl and phenyl moieties through carbon- or siliconbased bridges is currently limited to group 4 metal complexes that display phenyl coordination in 16e cations of the general formula $[(\eta^5:\eta^n-C_5H_4(bridge)Ph)M(R)_2]^{+.5}$

Following our interest in molybdenum and tungsten compounds supported by the bulky pentabenzylcyclopentadienyl ligand,⁶ we report now new cationic complexes of this family and demonstrate the ability of the pentabenzylcyclopentadienyl to behave as a chelating ligand through the additional η^2 -Ph bonding of one benzyl group. While electronrich metal complexes stabilize η^2 -arene coordination through metal to arene back-bonding to give C–H oxidative addition or arene dearomatization and further functionalization,⁷ the reverse situation, that is, acidic metal centers stabilized by intramolecular η^2 -arene bonding, is restricted. Relevant examples of these types of compounds are (i) $Cp(CO)W[\mu$ - $C(p-tolyl)(R)](\mu-CO)Pd(Cl)$, which presents a bridging alkylidene ligand where the p-tolyl group binds to the tungsten,⁸ (ii) $[CpMo(PPh_3)(CO)_2]^+$, which displays a η^2 -Ph interaction of one phenyl ring of the triphenylphosphine ligand with the metal,⁹ and (iii) $[(\eta^5:\eta^n-\hat{Cp}(bridge)\hat{Ph})M(\tilde{R})_2]^+$, where M = Ti, Zr and the bridge is a Me₂C fragment.⁵ Related examples, where arene coordination compensates for the electronic deficiency of an acidic metal center, are the reactions of [CpReH(NO)(CO)] with tropylium or trityl cations that lead to the formation of $[CpRe(NO)(CO)(\eta^2-arene)]$ (η^2 arene = η^2 -C₇H₈, η^2 -PhCHPh₂). The arene ligands in these reactions are formed in situ by reactions of the cations with the hydride ligand.¹⁰

The results reported here are closely connected to the catalytic activity displayed by $[MCp^{Bz}(CO)_3]^+$ in the ionic hydrogenation of ketones and further attest to the determining role of intramolecular interactions and fluxional processes offered by hemilabile ligands in catalysis. Among other factors previously discussed, the high activity displayed by

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 $[MCp^{Bz}(CO)_3]^+$ in comparison to that of $[MCp(CO)_3]^+$ and $[MCp(CO)_2(PMe_3)]^+$ is likely due to the ability of the pentabenzylcyclopentadienyl ligand to stabilize the unsaturated 16e molybdenum cation responsible for H_2 activation.^{6d,11}

RESULTS AND DISCUSSION

Synthesis and Reactivity. The stoichiometric addition of Ph_3CBAr_F ($BAr_F = B(3,5-C_6H_3(CF_3)_2)_4$) to the hydrides $[MCp^{Bz}(CO)_3H]$ (M = Mo(1), W(2); $Cp^{Bz} = pentabenzyl-cyclopentadienyl)$ in dichloromethane results in hydride transfer to the trityl cation and formation of the cationic complexes $[M\{\eta^5:\eta^2-C_5Bz_4CH_2Ph\}(CO)_3]BAr_F$ (M = Mo(3), W(4)), which are obtained in high yields (75% for 3 and 90% for 4) as dark purple and purple solids, respectively (Scheme 1).



The proton and carbon NMR spectra of 3 and 4 provide the evidence for their molecular structures. The spectra are diagnostic of C_s symmetry with a plane containing the methylene and the ipso carbons of the bridging benzyl group and crossing the C-C bond of the cyclopentadienyl ring that is opposite to the metal-coordinated phenyl ring. Thus, in the ¹H NMR spectra of both compounds, the methylenic protons of the five benzyl groups give rise to one singlet and to two AB systems, integrating for four protons each. The chemical shifts of the ortho protons of the bridging benzyl constitute further evidence for the coordination of the phenyl ring,^{5a} as they are displaced upfield (δ 6.51 ppm for 3 and δ 6.54 ppm for 4) in comparison to those for other pentabenzylcyclopentadienyl tricarbonyl complexes.^{6a,c-e} The ¹³C NMR spectra of 3 and 4 also support the coordination of the phenyl group to the metals, as evidenced by the broadening and upfield shift of the ortho carbon resonances (δ 102.1 ppm for 3 and δ 98 ppm for 4)⁹ and by the downfield shift of the meta carbon signals (δ 142.2 ppm for 3 and δ 144.3 ppm for 4) in comparison with other η^5 -Cp^{Bz} cationic carbonyl compounds.^{6a,c-e} Additionally, the carbon NMR spectra show two resonances above 200 ppm that are due to the carbonyl ligands (δ 232.5 and 227.4 ppm for 3 and δ 220.6 and 220.2 ppm for 4). The identification of 3 and

4 as ionic compounds was also confirmed by the ¹⁹F and ¹¹B NMR spectra, which show the characteristic resonances of BAr_F. The IR spectra show typical stretching bands for the carbonyl ligands at 2057 and 1978 cm⁻¹ for 3 and at 2050 and 1963 cm⁻¹ for 4. A comparison of the $\nu_{\rm CO}$ bands in 3 and 4 with those of the parent compounds^{6c} is consistent with the formation of cationic metal centers.

The magnetic equivalence of the ortho and meta protons of the bonded phenyl ring hints at a fluxional process corresponding to the equilibrium presented in Scheme 2.





Low-temperature ¹H NMR studies performed in a dichloromethane- d_2 solution of 3 showed that this process could not be stopped until -80 °C, as the only observed effect was the broadening of all resonances. This result is in accordance with a low activation energy barrier for the process, as confirmed by DFT calculations presented below.

The NOESY spectrum of complex 3 reveals cross-peaks between all ortho protons (see Figure 1). This result is



Figure 1. Aromatic region of the NOESY spectrum of 3 at 293 K, showing the cross-peaks between the ortho resonances of all benzyl groups for 3 (500 MHz, CD_2Cl_2 , mixing time 500 ms).

consistent with another fluxional process that can be attributed to an equilibrium exchange process in which each of the five phenyl groups are, in turn, coordinating to the metal. The exchange rate constants associated with this process were calculated from the intensities of 2D-EXSY peaks of the ortho protons at six different temperatures. As expected, the mechanism of the intramolecular exchange process is simple and the relaxation matrix contains only one exchange rate constants reported in Table 1, and the activation parameters $\Delta H^{\ddagger} = 14.9 \pm 0.4$ kcal mol⁻¹, $\Delta S^{\ddagger} = 16 \pm 1$ kcal mol⁻¹, and $\Delta G^{\ddagger}_{298} = 10.1 \pm 0.2$ kcal mol⁻¹ were obtained using the Eyring equation (see Figure 1S in the Supporting Information). The

Table 1. Exchange Rate Constants k for 3 at Different Temperatures^{*a*}

<i>T</i> (K)	$k (s^{-1})$	<i>T</i> (K)	$k (s^{-1})$	
290	0.18	301	0.53	
293	0.25	306	0.82	
296	0.32	312	1.19	
^a Errors in rate constants range from 5 to 10%.				

moderately high value of $\Delta G^{\ddagger}_{298}$ is in agreement with the formation of a labile Mo $-\eta^2$ -Ph bond in 3. The same dynamic process was not observed for the tungsten analogue 4, and the NOESY spectrum of a dichloromethane- d_2 solution of this compound at room temperature is compatible with a static coordination of one phenyl group as a consequence of a stronger metal-carbon bond.

Treatment of 1 and 2 with Ph_3CBF_4 in dichloromethane- d_2 results in the formation of the zwitterionic species $[MCp^{Bz}(CO)_3(FBF_3)]$ (M = Mo (5), W (6)), displayed in Scheme 1. This behavior, which is similar to that for other cyclopentadienyl analogues,¹² shows that when the counterion is a small coordinating anion the formation of the zwitterionic complexes is preferred over η^2 -phenyl coordination. It is significant that in the presence of BF₄⁻ the stabilization of the 16e cationic center through intramolecular coordination of one phenyl ring is not observed, while the coordination of the phenyl ring is favored when the bulky Ph3CBAr_F is used as hydride abstractor. The influence of counterions in the course of reactions is well documented as a determining factor in catalytic reactions;¹³ however, the formation of η^2 -arene species in hydride abstraction reactions has been observed only rarely^{9,12} and the compensation for the electronic unsaturation of metal centers is usually provided by the coordination of counterions or solvent molecules.¹² The situation reported here reflects the noncoordinating behavior of BAr_F, which is likely a consequence of steric factors. The bulkiness of the cyclopentadienyl ring and BAr_F forces this anion to stay away from the metal and compels the ansa-bridged coordination of the Cp^{Bz} ring to balance the electron deficiency of the metal center. The coordination of BF_4^- in 5 and 6 is supported by the ¹⁹F NMR data. At room temperature an exchange between the four fluorides of the BF_4^- ion justifies the equivalence of all fluorine resonances in 5; this process is stopped at -80 °C, leading to the splitting of each signal in three nonequivalent resonances.¹⁴ The exchange process is slower in the tungsten complex; two resonances corresponding to the bridging and to the terminal fluorides are observed at room temperature. A limit spectrum identical with that obtained for 5 is attained on cooling.

 $[M{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F (M= Mo (3), W (4))$ complexes are stable in the solid state at room temperature under an atmosphere of dry nitrogen. However, in CD₂Cl₂ solution the ¹H spectra start to display new resonances corresponding to about 1% decomposition after 1 day for 3 and 4 days for 4, which gradually increase with time. The NMR data for the new species are consistent with the occurrence of a carbonyl exchange reaction leading to the formation of $[MCp^{Bz}(CO)_4]BAr_F (M = Mo (7), W (8))$, which were identified by comparison of the NMR spectra with those of authentic samples obtained by reactions of 3 and 4 with CO (Scheme 3). In the absence of CO the formation of the tetracarbonyls is very slow, but it is immediate and quantitative when CO is added to dichloromethane solutions of 3 or 4. No other species are observed by NMR concomitantly with the





formation of 7 and 8 in CD₂Cl₂ solutions, and the ¹¹B and ¹⁹F NMR spectra also did not show any signals other than those assignable to BAr_F. This result may suggest that the fragment resulting from CO release decomposes through radical processes to paramagnetic species that are not detected by NMR. The formation of a few crystals of $[MoCp^{Bz}(CO)_3]_2$ after a few months in the NMR tube attests to the reduction of molybdenum and supports the occurrence of redox processes. This observation raised the question of the origin of CO. It is known that thermal decarbonylation of $[MCp^{Bz}(CO)_3]_2$ is a source of CO with formation of [MoCp^{Bz}(CO)₂]₂. ⁶ Therefore, reactions of $[Mo{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$ (3) with $[MoCp^{Bz}(CO)_3]_2$ in 2:1 and 1:1 ratios were carried out with the aim of assessing if the latter complex could be the origin of CO to form $[MoCp^{Bz}(CO)_4]BAr_F$. The results of these reactions were ambiguous because though the NMR spectra reveal the formation of 7 and also a residual amount of $[MoCp^{Bz}(CO)_2]_2$, the reactions led to other minor species that could not be identified. The ratio between 7 and $[MoCp^{Bz}(CO)_2]_2$ excludes $[MoCp^{Bz}(CO)_3]_2$ as being the only CO source for the formation of 7. It is clear that addition of $[MCp^{Bz}(CO)_3]_2$ to dichloromethane- d_2 solutions of [M- $\{\eta^5: \eta^2-C_5Bz_4CH_2Ph\}(CO)_3\}^+$ in a sealed tube accelerates the formation of $[MCp^{Bz}(CO)_4]^+$ and gives rise to the formation of small amounts of $[MCp^{Bz}(CO)_2]_2$ but the integration of the NMR spectra did not clarify the matter.

The ¹H NMR spectra of 7 and 8 display one set of resonances corresponding to the Cp^{Bz} ligand, and the ¹³C NMR spectra show only one resonance for the CO ligands, as expected for a four-legged piano-stool geometry. The IR spectra in KBr pellets show four strong ν_{CO} bands between 2110 and 1977 cm⁻¹ and between 2108 and 1957 cm⁻¹ for 7 and 8, respectively; however, in CH₂Cl₂ solutions each compound gives rise to only two bands (ν_{CO} 2109, 2034 cm⁻¹ for 7 and 2107, 2024 cm⁻¹ for 8). The observation of two bands in solution is in agreement with the free rotation of the Cp^{Bz} ligand and the $C_{4\nu}$ symmetry displayed by the complexes in solution and suggests that the high number of carbonyl bands in the solid state may be due to symmetry reduction associated with crystal packing. A comparison between the IR spectra of 7 and 8 with those of 3 and 4, respectively, also points out the stabilization conferred by the phenyl

coordination in the $\eta^5:\eta^2$ -pentabenzylcyclopentadienyl compounds and the highly acidic nature of the metal centers in the cationic tetracarbonyl complexes. Indeed, the CO stretching bands in 7 and 8 do not deviate notably from the value observed for free CO and are in accordance with the short carbon–oxygen distances revealed by the X-ray structures of $[MCp^{Bz}(CO)_4]BF_4$ discussed below.

The extreme solubility of 7 and 8 in ordinary solvents such as dichloromethane, toluene, and diethyl ether gives rise to very viscous solutions that hamper the formation of crystals suitable for X-ray characterization. However, crystals of $[MCp^{Bz}(CO)_4]$ -BF₄ (M = Mo (9), W (10)) suitable for X-ray diffraction (see below) were grown in the NMR tubes from CD_2Cl_2 solutions of $[MCp^{Bz}(CO)_3(FBF_3)]$ after some months. These results confirm that, in the absence of additional good donors, tetracarbonyl cationic species are decomposition products of cationic Mo and W pentabenzylcyclopentadienyl tricarbonyl complexes.

The stability of $[M{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$ (3 and 4) in air was tested. The ¹H NMR spectrum of 4 reveals no signals of decomposition when the complex is left in the solid state in air for several weeks. However a dichloromethane solution of 4 in open air shows 40% conversion to $[WCp^{Bz}(CO)_3(OH_2)]BAr_F$ (12) within 2 h. The molybdenum analogue 3 is, as expected, more sensitive; even in the solid state the conversion to $[MoCp^{Bz}(CO)_3(OH_2)]BAr_F$ (11) reaches about 50% after 3 h in air. Complexes 11 and 12 were independently prepared by reactions of 3 and 4 with water (Scheme 3). A color change from purple to orange is observed upon addition of an excess of degassed distilled water to dichloromethane solutions of 3 and 4. Evaporation of the solvent under vacuum gave initially red-orange oils that convert to purple solids on further exposure to vacuum. The ¹H NMR spectrum of the red-orange samples reveal the presence of variable amounts of the aqua complexes $[MCp^{Bz}(CO)_3(OH_2)]$ -BAr_F and $[M{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$. The formulation of 11 and 12 as the aqua adducts was mainly supported by the ¹H NMR and IR spectra. The proton NMR spectra in CD₂Cl₂ show broad resonances, at δ 4.99 ppm for 11 and δ 5.12 ppm for 12, accounting for the two protons of coordinated water, together with a broad peak at about δ 2 ppm associated with free water. The NOESY spectra display EXSY cross-peaks between free and coordinated water that are symptomatic of a slow exchange in solution. The chemical shifts observed for the water protons in 11 and 12 are shifted strongly downfield in relation to the values reported for the closely related complex $[MoCp(CO)_2(PPh_3)(OH_2)]BAr_F$ (2.87 < δ_{H_2O} < 3.31 ppm), described by Bullock and co-workers.¹⁵ Despite the fact that the proton chemical shifts of coordinated water habitually suffer large displacements, mainly related to fluxional processes that depend on the solvents and free water content, the difference noted above reflects the highly acidic nature of the metal centers in 11 and 12 due to the presence of one extra carbonyl instead of a phosphine ligand.

The reversibility of the hydration reactions was confirmed by NMR, as the only species observed after exposure of the mixtures to prolonged vacuum were the starting compounds $[M{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$. The lability of water contrasts with the static behavior of 7 and 8, for which no displacement of CO was registered even after many hours under vacuum.

X-ray Diffraction. Complexes 9 and 10 are isomorphous and crystallize in the $P\overline{1}$ space group with a cocrystallized dichloromethane molecule. The molecular structure of 10 (Figure 2) illustrates the structures of both complexes, and relevant bond distances and angles for 9 and 10 are presented in Table 2.



Figure 2. Molecular structure of **10** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms, BF_4^- , and CH_2Cl_2 are omitted for clarity.

Table 2.	Selected	Bond	Lengths	(Å)	and	Angles	(deg)	for 9
and 10			•					

	9	10
	Distances (Å)	
M-Cp ^{Bz} _{CT}	1.9904(11)	1.9936(10)
M-C(6)	2.052(3)	2.035(3)
M-C(7)	2.043(3)	2.032(3)
M-C(8)	2.047(3)	2.051(2)
M-C(9)	2.051(3)	2.030(3)
C(6) - O(1)	1.123(3)	1.132(3)
C(7) - O(2)	1.127(3)	1.138(3)
C(8) - O(3)	1.123(3)	1.120(3)
C(9) - O(4)	1.127(3)	1.138(3)
	Angles (deg)	
$Cp^{Bz}_{CT}-M-C(6)$	117.50(8)	118.86(8)
$Cp^{Bz}_{CT} - M - C(7)$	116.69(8)	124.55(8)
$Cp^{Bz}_{CT}-M-C(8)$	118.81(8)	117.60(7)
$Cp^{Bz}_{CT} - M - C(9)$	124.26(9)	116.94(8)
M - C(6) - O(1)	177.8(2)	177.4(2)
M - C(7) - O(2)	176.0(2)	176.7(2)
M - C(8) - O(3)	177.8(2)	177.6(2)
M - C(9) - O(4)	176.2(2)	175.8(2)
C(6)-M-C(7)	77.74(10)	75.65(10)
C(7)-M-C(8)	77.25(11)	73.89(10)
C(8)-M-C(9)	76.07(11)	77.44(10)
C(9)-M-C(6)	73.60(10)	77.10(10)

In both compounds the cationic fragments have the typical four-legged piano-stool geometry with distances between the metals and the ring centroids $(M-Cp^{Bz}_{CT})$ of 1.9904(11) and 1.9936(10) Å in 9 and 10, respectively. As is usually observed in pentabenzylcyclopentadienyl complexes four benzyl substituents are directed above the Cp ring planes and one points down toward the metals. The metal–carbonyl bond lengths are slightly elongated and the C–O distances are shortened in

comparison to those in $[MCp^{Bz}(CO)_3H]$.^{6c} The C–O bond lengths (ranging from 1.123(3) to 1.127(3) Å for 9 and from 1.120(3) to 1.138(3) Å for 10) are very close to the value reported for free carbon monoxide (1.128 Å), thus corresponding to C=O bonds. These features reflect the competition of four CO ligands to the metal to ligand back-bonding, which is restricted in consequence of the cationic charge of the compounds. In general the structural parameters obtained for 9 and 10 agree with those for other half-sandwich molybdenum and tungsten carbonyl complexes.^{6,16,17}

DFT Calculations. The experimental results described above were further complemented by computational studies obtained by means of DFT calculations (see Computational Details).¹⁸ Thus, complex 3^+ , $[Mo\{\eta^5:\eta^2-C_5Bz_4CH_2Ph\}-(CO)_3]^+$, was the subject of a geometry optimization in order to clarify the nature of the interaction between the metal and the coordinated benzyl group of the Cp^{Bz} ligand. In the calculated structure (see Figure 3) the coordination of the



Figure 3. Enthalpy profile (PBE0, kcal mol⁻¹) calculated for the fluxional process involving the coordinated phenyl group in 3^+ . The optimized geometries are represented with the coordinated benzyl group and the Mo(CO)₃ fragment highlighted. The relevant Mo–C distances (Å) are indicated.

benzyl group via the ortho C atom is evident. The corresponding Mo– C_{ortho} distance of 2.57 Å is indicative of an attractive interaction, as is further corroborated by a Wiberg index (WI)¹⁹ of 0.21. The geometry constraints imposed by the five-membered metallacycle in 3⁺ (Mo– C_{Cp} – C_{CH_2} – C_{ipso} – C_{ortho}) push the ipso C atom away from the metal (d_{Mo-C} = 2.95 Å), weakening the corresponding Mo–C bond (WI = 0.06) and resulting in what may be viewed as a very distorted coordination of a double bond (C_{ipso} = C_{ortho}).

The stabilization achieved by coordination of the phenyl group in 3^+ was evaluated by a comparison between 3^+ and a putative intermediate with none of the phenyl groups coordinating the metal, $[Mo(\eta^5-C_5Bz_5)(CO)_3]^+$ (A; see Figure S2 in the Supporting Information). Cation 3^+ is more stable than this intermediate by $\Delta H = 24.3$ kcal mol⁻¹, providing a clear indication of the stability gained by the complex through the coordination of the phenyl group. In addition, that enthalpy

value excludes this intermediate from the mechanism of exchange between the five phenyl groups discussed above, since the experimental activation enthalpy measured by NMR for this process ($\Delta H^{\ddagger} = 14.9$ kcal mol⁻¹, see Figure S1 in the Supporting Information) is considerably lower than the enthalpy splitting between 3⁺ and **A**. Thus, the exchange mechanism is probably concerted, with every new phenyl coordination causing the cleavage of the previous one and avoiding, in this way, an unstable intermediate such as **A**.

In summary, the calculations confirm that the electron deficiency on the metal, created by the loss of the hydride in the original complex, is compensated by the coordination of one benzyl substituent of the Cp^{Bz} ligand. In this way, the cation $[Mo{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]^+$ (3⁺) is able to maintain a formal electron count of 18.

The mechanism of the fluxional process involving the coordinated benzyl group was also investigated. That process was observed by NMR (see Scheme 2) and makes both sides of the coordinated phenyl ring equivalent. The corresponding enthalpy profile is represented in Figure 3, along with the optimized structures for the relevant species.

The fluxional process occurs in a single step, going over a transition state (**TS**) in which coordination of the phenyl group is totally symmetric, as shown by two equal Mo-C_{ortho} distances of 3.21 Å. These correspond to weak interactions (WI = 0.05), indicating that one $Mo-C_{ortho}$ bond is practically broken before the other one starts to form along the fluxional process. In the transition state (TS) the electron loss in the metal center due to the weakening of the $Mo-C_{ortho}$ bond is partially balanced by a strengthening of the interaction between the metal and the ipso C atom ($d_{Mo-C} = 2.77$ Å, WI = 0.12). This reinforcement of the C_{ipso} coordination, in TS, is made possible by the release of steric constraint in the metallacycle, being a consequence of the elongation of the $Mo-C_{ortho}$ distance. Most importantly, the barrier calculated ($\Delta H^{\ddagger} = 8.8$ kcal mol⁻¹) corroborates a facile process that could not be stopped in the temperature range employed in the NMR studies (see above), being considerably smaller than the experimental value obtained for the exchange of a coordinated phenyl group.

The mechanism of fluxionality of the coordinating phenyl group was also calculated for the tungsten complex 4^+ . The enthalpy barrier obtained, $\Delta H^{\ddagger} = 9.4$ kcal mol⁻¹, is higher than that calculated for 3^+ , as expected on going from a Mo to a W complex, but is also small enough to justify that the process cannot be stopped in the temperature range employed in the NMR experiments, in agreement with the experimental observations.

The stabilization of the 16-electron fragment $[MCp^{Bz}(CO)_3]^+$, which results from hydride loss in the original complexes $[MCp^{Bz}(CO)_3H]$ (1 and 2), can also be achieved through coordination of one extra ligand, as shown by the experimental results discussed above. Neutral 2-electron donors (L) yielded cations, $[MCp^{Bz}(CO)_3L]^+$, such as the aqua complexes (L = H₂O, 11⁺ and 12⁺), or the tetracarbonyl species $[MCp^{Bz}(CO)_4]^+$ (7⁺-10⁺). The BF₄⁻ counterion also coordinates to the metal, forming the zwitterionic complexes **5** and **6**. The corresponding reactions of addition of one extra ligand to $[Mo\{\eta^5:\eta^2-C_5Bz_4CH_2Ph\}(CO)_3]^+$ (3⁺) were studied by DFT, and the enthalpy balances obtained are summarized in Figure 4.

The most favorable reaction among all addressed in Figure 4 is CO addition with formation of the tetracarbonyl complex



Figure 4. Enthalpy balance calculated (PBE0, kcal mol^{-1}) for the addition of one extra ligand to 3^+ .

 $[MoCp^{Bz}(CO)_4]^+$ (7⁺/9⁺). The calculated energy balance ($\Delta H = -13.8 \text{ kcal mol}^{-1}$) indicates a stable product, in excellent agreement with the experimental results discussed above. In fact, CO addition to the tricarbonyl species is a nonreversible reaction and, in addition, the tetracarbonyl complexes 7⁺-10⁺ are the final decomposition products observed for the tricarbonyl species.

Another interesting result is the rather small absolute value calculated for the enthalpy balance of the hydration reaction $(\Delta H = -1.3 \text{ kcal mol}^{-1})$. This result agrees well with the reversible character experimentally observed for this reaction and with the establishment of an equilibrium between the two complexes $[Mo\{\eta^5:\eta^2\cdot C_5Bz_4CH_2Ph\}(CO)_3]^+$ and $[MoCp^{Bz}(CO)_3(OH_2)]^+$. Thus, binding of the water molecule replaces the benzyl group in the metal coordination sphere but no significant stabilization is achieved with this process.

An enthalpy balance of $\Delta H = -12.6 \text{ kcal mol}^{-1}$, obtained for the formation of the zwitterionic species $[\text{MoCp}^{\text{Bz}}(\text{CO})_3(\text{FBF}_3)]$ (5), corroborates its formation as experimentally identified. In fact, the small size and hard donor properties of the BF₄⁻ anion allows its coordination to the metals and stabilization of the resulting tricarbonyl species through formation of $[\text{MoCp}^{\text{Bz}}(\text{CO})_3(\text{FBF}_3)]$ (M = Mo (5), W (6)). On the other hand, if the anion is the bulkier and noncoordinative BAr₄⁻, the corresponding adduct is not formed and the previous process does not occur. Metal stabilization has to be attained through benzyl coordination, following the necessary rearrangement on the Cp^{Bz} ligand conformation.

CONCLUDING REMARKS

The work described reveals new facets of half-sandwich molybdenum and tungsten carbonyls. The intramolecular coordination of one phenyl ring of the pentabenzylcyclopentadienyl ligand follows hydride abstraction from $[MCp^{Bz}(CO)_3H]$ (M = Mo, W) when a trityl salt of a bulky noncoordinating anion is used. The coordination of the ansabridging benzyl group to Mo is fluxional, involving an exchange between the five benzyl groups for metal binding, but its bonding in the W analogue is static at room temperature, on the NMR time scale. The rate constants and the activation parameters for the exchange process have been determined from the intensities of 2D-EXSY peaks of the ortho protons.

The use of Ph_3CBF_4 as a hydride abstractor results in borate coordination and formation of zwitterionic complexes. The results reported here point out that the cationic species formed upon hydride abstraction depend on the balance between the steric properties of the starting complex and the counterion.

The stabilization achieved by the intramolecular coordination of the phenyl ring in the absence of other donors may be responsible for the different activities of $[MoCp'(CO)_3]^+$ systems (Cp' = C₅Bz₅, C₅H₅) in the ionic hydrogenation of ketones.^{6d,11} Among other aspects related to fine electronic differences between the two systems,^{6d} the much higher activity of the pentabenzylcyclopentadienyl system is likely related to the η^2 -Ph bonding that may support the regeneration of the catalyst $[MoCp'(CO)_3(H)_2]^+$ upon reaction of the tricarbonyl cations with H₂.

$$\begin{split} & [W\{\eta^{5}:\eta^{2}\text{-}C_{5}Bz_{4}CH_{2}Ph\}(CO)_{3}]BAr_{F} \text{ is stable in air in the solid state. In solution } [M\{\eta^{5}:\eta^{2}\text{-}C_{5}Bz_{4}CH_{2}Ph\}(CO)_{3}]BAr_{F} (M = Mo, W) \text{ reacts readily with } H_{2}O, \text{ which displaces the metal-coordinated phenyl group to give the corresponding aqua adducts. The hydration reaction may be quantitatively reverted under vacuum. } [M\{\eta^{5}:\eta^{2}\text{-}C_{5}Bz_{4}CH_{2}Ph\}(CO)_{3}]BAr_{F} \text{ and } [MCp^{Bz}(CO)_{3}(FBF_{3})] \text{ convert slowly to } [MCp^{Bz}(CO)_{4}]BX_{4} (X = Ar_{F}, F) \text{ in dicloromethane solutions. The simultaneous formation of } [MCp^{Bz}(CO)_{3}]_{2}, \text{ observed by NMR, suggests a disproportionation process. The tetracarbonyl cations } [MCp^{Bz}(CO)_{4}]BX_{4} (M = Mo, W; X = Ar_{F}, F) \text{ display a fourlegged piano-stool geometry and are very stable toward CO loss.} \end{split}$$

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under dry nitrogen by using standard Schlenk and high vacuum line techniques or in a nitrogen-filled glovebox. Dichloromethane and nhexane were predried using 4 Å molecular sieves and freshly distilled from CaH₂ under a nitrogen atmosphere. Dichloromethane-d₂ was dried with activated 4 Å molecular sieves, degassed by freeze-pumpthaw cycles, and stored under an atmosphere of nitrogen. The compounds $[MCp^{Bz}(CO)_{3}H]$ (M = Mo (1), W (2))^{6c} and $Ph_3CBAr_F^{20}$ were prepared according to published procedures. Carbon monoxide (purity 99.997% CO-N47) was purchased from Air Liquide Portugal. NMR spectra were recorded on Bruker AVANCE 300, 400, and 500 MHz MHz spectrometers at 296 K, unless stated otherwise. ¹H NMR spectra were referenced internally to the residual proton solvent resonances relative to tetramethyl
silane (dichloromethane- $d_{2},\,\delta$ 5.32 ppm), ¹³C{¹H} NMR spectra were referenced internally to the residual solvent resonances (dichloromethane- d_2 , δ 54.0 ppm), ¹⁹F NMR spectra were referenced externally to CF₃COOH (δ -76.55 ppm), and ¹¹B NMR spectra were referenced externally to BF₃·Et₂O $(\delta 0 \text{ ppm})$; proton and carbon assignments were made using HSQC, COSY, NOESY, and HMBC 2-D NMR experiments. Infrared spectra were recorded on a Jasco FI/IR-4100 spectrophotometer. Elemental

Table 3. Crystallographic Data for 9 and 10

	9	10
empirical formula	C.,HaBClaF.MoO.	C., H., BCLEO.W
formula wt	895.40	983.31
temp (K)	150	150
wavelength (Å)	0.710 73	0.710 73
cryst syst	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$
unit cell dimens		
a (Å)	9.8453(4)	9.8487(3)
b (Å)	10.2772(4)	10.2715(3)
c (Å)	19.8022(8)	19.8080(6)
α (deg)	97.231(2)	97.230(2)
β (deg)	91.260(2)	91.264(2)
γ (deg)	95.104(2)	95.034(2)
V (Å ³)	1978.69(14)	1979.08(10)
Ζ	2	2
calcd density (Mg m ⁻³)	1.503	1.650
abs coeff (mm ⁻¹)	0.530	3.117
F(000)	912	976
cryst size (mm)	$0.02\times0.10\times0.25$	$0.10 \times 0.10 \times 0.10$
θ range for data collection (deg)	2.35-25.40	2.75-30.12
limiting indices	$-11 \le h \le 11, -12 \le k \le 11, -19 \le l \le 23$	$-13 \le h \le 13, -14 \le k \le 14, -27 \le l \le 27$
no. of collected/ unique rflns $[R_{int}]$	26 950/7220 [0.0457]	57 051/11 533 [0.0416]
completeness to θ (%)	98.9 (θ = 25.40)	98.9 (θ = 30.12)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/ restraints/params	7220/0/514	11 533/0/514
goodness of fit on F^2	1.036	1.040
final <i>R</i> indices $(I > 2\sigma(I))^a$	R1 = 0.0361, wR2 = 0.0780	R1 = 0.0263, wR2 = 0.0592
R indices (all data) ^{a}	R1 = 0.0514, wR2 = 0.0819	R1 = 0.0320, wR2 = 0.0606
abs cor	multiscan	multiscan
largest diff peak/ hole (e Å ⁻³)	0.647 and -0.627	1.503 and -0.819
${}^{a}\mathrm{R1} = \sum_{v} F_{o} - \sum_{v} [w(F_{o}^{2})^{2}] \}^{1/2}.$	$ F_{\rm c} /\sum F_{\rm o} ;$ wR2 =	$\{\sum [w(F_o^2 - F_c^2)^2]/$

analyses were performed by Laboratório de Análises of IST, Lisbon, Portugal.



[Mo{ $\eta^5:\eta^2-C_5Bz_4CH_2Ph$ }(CO)₃]BAr_F (3). To a dichloromethane solution of [MoCp^{Bz}(CO)₃H] (1; 0.360 g, 0.52 mmol) at 0 °C was added dropwise a solution of Ph₃CBAr_F (0.571 g, 0.52 mmol) in the same solvent. The solution changed immediately from pale yellow to dark red-brown. The reaction mixture was stirred at 0 °C for 2 h and then at room temperature for a further 3 h. The solvent was removed under vacuum, leading to a dark red-brown oil that became a solid after a while under vacuum. The solid was washed several times with *n*hexane to remove Ph₃CH and dried under vacuum to give 3 as a dark purple solid (0.390 g, 75% yield). ¹H NMR (CD₂Cl₂, 500.1 MHz, 296 K): δ (ppm) 7.96 (t, 2H, ${}^{3}J_{HH} =$ 7.4 Hz, m-Ph^A), 7.80 (t, 8H, o-Ph of BAr_F), 7.61 (s, 4H, p-Ph of BAr_F), 7.47 (t, 1H, ${}^{3}J_{HH} = 7.8$ Hz, p-Ph^A), 7.37-7.31 (overlapping, 6H total, 4H, m-Ph^B, 2H, p-Ph^B), 7.12 (t, 2H, p-Ph^C), 7.07-7.04 (overlapping, 8H total, 4H, m-Ph^C, 4H, o-Ph^B), 6.75 (m, 4H, o-Ph^C), 6.51 (d, 2H, ${}^{3}J_{HH} = 6.4$ Hz, o-Ph^A), 3.96 (d, 2H, ${}^{2}J_{\text{HH}} = 17 \text{ Hz}, CH_{2}{}^{B/B}\text{Ph}^{B}$, 3.86 (d, 2H, ${}^{2}J_{\text{HH}} = 17 \text{ Hz}, CH_{2}{}^{B/B}\text{Ph}^{B}$), 3.78 (d, 2H, ${}^{2}J_{HH} = 16$ Hz, $CH_{2}^{C/C}Ph^{C}$), 3.58 (d, 2H, ${}^{2}J_{HH} = 16$ Hz, CH₂^{Ci/C}Ph^C), 3.58 (s, 2H, CH₂^APh^A). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 296 K): δ (ppm) 232.5 (CO), 227.4 (CO), 162.2 (q, ${}^{4}J_{CB} = 50$ Hz, *i*-Ph of BAr_F), 142.2 (*m*-Ph^A), 136.4 (*i*-Ph^B or *i*-Ph^C), 136.3 (*i*-Ph^B or *i*-Ph^C), 135.2 (s, *o*-Ph of BAr_F), 131.0 (*i*-Ph^A), 129.5 (qm, ${}^{2}J_{CF} = 30$ Hz, m-Ph of BAr_E), 129.9 (m-Ph^B), 129.4 (o-Ph^B), 128.8 (o-Ph^C), 128.7 (m-Ph^C), 128.5 (p-Ph^A), 128.4 (p-Ph^B), 128.2 (p-Ph^C), 125.0 (q, ${}^{1}J_{CF} = 272$ Hz, CF₃ of BAr_F), 117.9 (m, ${}^{3}J_{CF} = 4$ Hz, p-Ph of BAr_F), 114.6 (Cp^C), 111.6 (Cp^B), 106.1 (Cp^A), 102.1 (*o*-Ph^A), 32.9 (C^CH₂Ph), 30.4 (C^BH₂Ph), 29.6 (C^AH₂Ph). ¹⁹F{¹H} NMR (CD₂Cl₂) 282.4 MHz, 296 K): δ (ppm) -62.8 (s, CF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) -6.6 (m). IR (CH₂Cl₂): ν _{CO} 2057, 1978 cm⁻¹. Anal. Calcd for C₇₅H₄₇BF₂₄MoO₃: C, 57.68; H, 3.04. Found: C, 57.90; H. 2.96

 $[W{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$ (4). The compound was prepared from $[WCp^{Bz}(CO)_{3}H]$ (2; 0.341 g, 0.43 mmol) following the procedure described above for 3. Compound 4 was obtained as a purple solid in 90% yield (0.640 g). ¹H NMR (CD₂Cl₂, 500.1 MHz, 296 K): δ (ppm) 8.05 (t, 2H, ${}^{3}J_{HH} = 7.3$ Hz, m-Ph^A), 7.75 (t, 8H, o-Ph of BAr_F), 7.58 (s, 4H, p-Ph of BAr_F), 7.39-7.29 (overlapping, 7H total, 1H, p-Ph^A 4H, m-Ph^B, 2H, p-Ph^B), 7.11 (t, 2H, p-Ph^C), 7.05– 7.02 (overlapping, 8H total, 4H, m-Ph^C, 4H, o-Ph^B), 6.72 (m, 4H, o-Ph^C), 6.54 (d, 2H, ${}^{3}J_{HH} = 6.4$ Hz, o-Ph^A), 3.95 (d, 2H, ${}^{2}J_{HH} = 17$ Hz, ${}^{2}J_{H} = 17$ Hz, ${}^{2}J_{H} = 17$ Hz, ${}^{2}J_{H} = 17$ Hz, ${}^{2}J_$ $CH_2^{B/B}Ph^B$), 3.88 (d, 2H, ${}^2J_{HH} = 17$ Hz, $CH_2^{B/B}Ph^B$), 3.87 (d, 2H, ${}^2J_{HH} = 16$ Hz, $CH_2^{C/C}Ph^C$), 3.66 (d, 2H, ${}^2J_{HH} = 16$ Hz, $CH_2^{C/C}Ph^C$), 3.61 (s, 2H, CH₂^APh^A). ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz, 296 K): δ (ppm) 220.6 (CO), 220.2 (CO), 162.2 (q, ${}^{4}J_{CB}$ = 50 Hz, *i*-Ph of BAr_F), 144.3 (*m*-Ph^A), 136.9 (*i*-Ph^B or *i*-Ph^C), 136.8 (*i*-Ph^B or *i*-Ph^C), 135.6 (*i*-Ph^A), 135.4 (s, *o*-Ph of BAr_F), 130.0 (*m*-Ph^B), 129.5 (qm, ${}^{2}J_{CF}$ = 30 Hz, m-Ph of BAr_F), 129.5 (m-Ph^C), 128.9 (o-Ph^C), 128.5 (p-Ph^B), 128.4 (*p*-Ph^A), 128.3 (*p*-Ph^C), 127.8 (*o*-Ph^B), 125.2 (q, ${}^{1}J_{CF} = 272$ Hz, CF_3 of BAr_F), 118.1 (m, ${}^{3}J_{CF} = 4$ Hz, p-Ph of BAr_F), 111.2 (Cp^C), 110.0 (Cp^B), 103.7 (Cp^A), 98 (vb, *o*-Ph^A), 33.3 (C^CH₂Ph), 31.0 (C^BH₂Ph), 29.8 (C^AH₂Ph). ¹⁹F{¹H} NMR (CD₂Cl₂, 282.4 MHz, 296 K): δ (ppm) -62.8 (s, CF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) -6.6 (m). IR (CH₂Cl₂): ν_{CO} 2050, 1963 cm⁻¹. Anal. Calcd for C₇₅H₄₇BF₂₄WO₃: C, 54.70; H, 2.88. Found: C, 54.61; H, 2.81.

[**MoCp^{Bz}(CO)₃(FBF₃)] (5).** A dichloromethane solution of Ph₃CBF₄ (0.37 g, 1.10 mmol) was slowly added to a solution of $\left[\text{MoCp}^{\breve{Bz}}(\text{CO})_{3}\text{H}\right]$ (1; 0.78 g, 1.10 mmol) in the same solvent. A color change from yellow to reddish was observed immediately. The mixture was allowed to react for about 1 h, and the solvent was removed to dryness. The residue was washed with hexane to remove Ph₃CH and dissolved again in CH₂Cl₂ and filtered. The solvent was evaporated almost completely under vacuum, leading to the formation of a red solid. Hexane (3 mL) was added dropwise, and the solution was filtered off. The solid was dried under vacuum. Yield: 79% (0.68 g). The reaction was also performed in a J. Young valve NMR tube in dichloromethane- d_2 using Ph₃CBF₄ (0.020 g, 0.061 mmol) and $[MoCp^{Bz}(CO)_3H]$ (1; 0.042 g, 0.061 mmol). For this reaction, the NMR spectra revealed that 5 and Ph₃CH were the unique species in solution. ¹H NMR (CD₂Cl₂, 500.1 MHz, 296 K): δ (ppm) 7.16–7.10 (overlapping, 15H total, 10H, m-Ph, 5H, p-Ph), 6.84 (m, 10H, o-Ph), 3.73 (s, 10H, CH₂Ph). ¹³C{¹H} NMR (CD₂Cl₂, 125.6 MHz, 296 K): δ (ppm) 244.9 (CO), 226.6 (CO), 137.8 (i-Ph), 129.0 (o-Ph), 128.9 (m-Ph), 127.4 (*p*-Ph), 118.0 (C_5Bz_5), 32.2 (CH_2Ph). ¹⁹F{¹H} NMR $(CD_2Cl_2, 282.4 \text{ MHz}, 193 \text{ K}): \delta$ (ppm) -152.97 (d, $^2J_{FF} = 93.7 \text{ Hz},$ $(\mu$ -F)¹⁰BF₃), -153.04 (d, ²J_{FF} = 93.7 Hz, $(\mu$ -F)¹¹BF₃), -338.24 (q, ²J_{FF} = 92.1 Hz, $(\mu$ -F)BF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) -0.72 (s, FBF₃). IR (CH₂Cl₂), ν_{CO} 2064, 1991, 1932 cm⁻¹; ν_{B-F} 1126, 848, 713 cm⁻¹. Anal. Calcd for C₄₃H₃₅BF₄MoO₃: C, 66.00; H, 4.51. Found: C, 65.78; H, 4.38.

[WCp^{Bz}(CO)₃(FBF₃)] (6). Compound **6** was prepared by the same procedures described for **5**. With Ph₃CBF₄ (1.10 g, 2.13 mmol) and [WCp^{Bz}(CO)₃H] (1; 1.85 g, 2.13 mmol) as starting materials, **6** was isolated in 89% yield (1.64 g). ¹H NMR (CD₂Cl₂, 300.1 MHz, 296 K): δ (ppm) 7.10–7.06 (overlapping, 15H total, 10H, *m*-Ph, 5H, *p*-Ph), 6.79 (m, 10H, *o*-Ph), 3.85 (s, 10H, CH₂Ph). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 296 K): δ (ppm) 231.8 (CO), 222.1 (CO), 138.0 (*i*-Ph), 129.0 (*o*-Ph), 128.9 (*m*-Ph), 127.4 (*p*-Ph), 115.1 (C₅Bz₅), 32.3 (CH₂Ph). ¹⁹F{¹H} NMR (CD₂Cl₂, 282.4 MHz, 296 K): δ (ppm) –151.3 (br, (μ-F)BF₃), -365.7 (br,(μ-F)BF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) 0.74 (br, FBF₃). IR (CH₂Cl₂), ν_{CO} 2074, 2009, 1947 cm⁻¹; ν_{B-F} 1101, 874, 713 cm⁻¹. Anal. Calcd for C₄₃H₃₅BF₄WO₃: C, 59.34; H, 4.05. Found: C, 59.69; H, 4.32.

 $[MoCp^{Bz}(CO)_4]BAr_F$ (7). A dichloromethane- d_2 solution of [Mo- $\{\eta^5: \eta^2-C_5Bz_4CH_2Ph\}(CO)_3]BAr_F$ (3; 0.046 g, 0.030 mmol) was transferred to a J. Young valve NMR tube. The solution was then frozen in liquid nitrogen, evacuated on a vacuum line, and sparged with carbon monoxide. Upon warming to room temperature the solution turned yellow within 5 min. Evaporation of the solvent under vacuum gave 7 as a dark golden solid in quantitative yield. ¹H NMR (CD₂Cl₂, 300.1 MHz, 296 K): δ (ppm) 7.77 (t, 8H, o-Ph of BAr_F), 7.59 (s, 4H, p-Ph of BAr_F), 7.22-7.16 (overlapping, 15H total, 10H, *m*-Ph, 5H, *p*-Ph), 6.85 (m, 10H, *o*-Ph), 3.98 (s, 10H, CH₂Ph). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 296 K): δ (ppm) 216.4 (CO), 162.4 (q, ${}^{4}J_{CB} = 50$ Hz, *i*-Ph of BAr_F), 137.3 (*i*-Ph), 135.4 (s, *o*-Ph of BAr_F), 129.9 (*m*-Ph), 129.5 (qm, ${}^{2}J_{CF}$ = 30 Hz, *m*-Ph of BAr_F), 128.7 (*p*-Ph), 128.7 (o-Ph), 125.2 (q, ${}^{1}J_{CF} = 272$ Hz, CF₃ of BAr_F), 118.6 ($C_{5}Bz_{5}$), 118.1 (m, ${}^{3}J_{CF} = 4$ Hz, p-Ph of BAr_F), 32.5 (CH₂Ph). ${}^{19}F{}^{1}H$ NMR $(CD_2Cl_2, 282.4 \text{ MHz}, 296 \text{ K}): \delta$ (ppm) -62.7 (s, CF₃). ¹¹B NMR $(CD_2Cl_2, 96.3 \text{ MHz}, 296 \text{ K}): \delta (\text{ppm}) - 6.6 (\text{m}). \text{ IR: KBr pellet, } \nu_{CO}$ 2110, 2058, 2036, 1977 cm⁻¹; CH₂Cl₂, 2109, 2034 cm⁻¹. Anal. Calcd for C₇₆H₄₇BF₂₄MoO₄: C, 57.52; H, 2.98. Found: C, 57.24; H, 2.69.

 $[WCp^{Bz}(CO)_{4}]BAr_{F}$ (8). The compound was prepared from $[W{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$ (4; 0.045 g, 0.027 mmol) following the procedure described above for 7. An orange solution was obtained after 1 h at room temperature. Evaporation of the solvent under vacuum gave 8 as a dark orange solid in quantitative yield. ¹H NMR (CD₂Cl₂, 400.1 MHz, 296 K): δ (ppm) 7.77 (t, 8H, o-Ph of BAr_F), 7.60 (s, 4H, *p*-Ph of BAr_F), 7.24–7.16 (overlapping, 15H total, 10H, m-Ph, 5H, p-Ph), 6.84 (m, 10H, o-Ph), 4.04 (s, 10H, CH₂Ph). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz, 296 K): δ (ppm) 203.9 (CO), 162.4 (q, ${}^{4}J_{CB} = 50$ Hz, *i*-Ph of BAr_F), 137.3 (*i*-Ph), 135.4 (s, *o*-Ph of BAr_F), 129.9 (*m*-Ph), 129.5 (qm, ${}^{2}J_{CF}$ = 30 Hz, *m*-Ph of BAr_F), 128.7 (p-Ph), 128.7 (o-Ph), 125.2 (q, ${}^{1}J_{CF} = 272$ Hz, CF_{3} of BAr_{F}), 118.1 (m, ${}^{3}J_{CF} = 4$ Hz, p-Ph of BAr_F), 116.6 (C₅Bz₅), 32.6 (CH₂Ph). ${}^{19}F{}^{1}H{}$ NMR (CD₂Cl₂, 282.4 MHz, 296 K): δ (ppm) -62.7 (s, CF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) –6.6 (m). IR: KBr pellet, $\nu_{\rm CO}$ 2108, 2049, 2026, 1957 cm⁻¹; CH_2Cl_2 , 2107, 2024 cm⁻¹. Anal. Calcd for C76H47BF24WO4: C, 54.50; H, 2.83. Found: C, 54.43; H, 2.45

[MoCp^{Bz}(CO)₃(H₂O)]BAr_F (11). A dichloromethane- d_2 solution of $[Mo{\eta^{5:\eta^2-C_5}Bz_4CH_2Ph}(CO)_3]BAr_F$ (3; 0.040 g, 0.026 mmol) was transferred to a J. Young valve NMR tube, and an excess of previously degassed distilled water (5 µL, 0.28 mmol) was added at room temperature. Immediately a dark orange solution was obtained. NMR characterization revealed the formation of 11 in 70% yield. ¹H NMR (CD₂Cl₂, 400.1 MHz, 296 K): δ (ppm) 7.75 (t, 8H, *o*-Ph of BAr_F), 7.59 (s, 4H, *p*-Ph of BAr_F), 7.20–7.13 (overlapping, 15H total, 10H, *m*-Ph, 5H, *p*-Ph), 6.86 (m, 10H, *o*-Ph), 4.99 (br, 2H, Mo–OH₂), 3.74 (s, 10H, CH₂Ph), 2.47 (br, free H₂O). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz, 296 K): δ (ppm) 23.86 (CO), 226.3 (CO), 162.4 (q, ⁴J_{CB} = 50 Hz, *i*-Ph of BAr_F), 137.5 (*i*-Ph), 135.4 (s, *o*-Ph of BAr_F), 129.5 (m, ²J_{CF} = 30 Hz, *m*-Ph of BAr_F), 129.0 (*o*-Ph), 128.1 (*p*-Ph), 125.2 (q, ¹J_{CF} = 272 Hz, CF₃ of BAr_F), 118.1 (m, ³J_{CF} = 4 Hz, *p*-Ph of BAr_F), 117.7 (C₅Bz₅), 32.5 (CH₂Ph). ¹⁹F{¹H} NMR (CD₂Cl₂, 282.4 MHz, 296 K): δ (ppm) –62.8 (s, CF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) –66. (m). IR (KBr pellet): ν_{OH} 3677 and 3619 cm⁻¹ (w, br).

 $[WCp^{Bz}(CO)_3(H_2O)]BAr_F$ (12). An excess of previously degassed distilled water (16 μ L, 0.89 mmol) was added to a dichloromethane

solution of $[W{\eta^5:\eta^2-C_5Bz_4CH_2Ph}(CO)_3]BAr_F$ (4; 0.104 g, 0.063 mmol) at room temperature, with vigorous stirring. After 5 min the violet solution had changed to red-orange. The mixture was stirred for $1/_{2}$ h, followed by evaporation of the solvent under vacuum to give 12 as a red-orange oil in 45% yield. ¹H NMR (CD₂Cl₂, 400.1 MHz, 296 K): δ (ppm) 7.74 (t, 8H, o-Ph of BAr_F), 7.57 (s, 4H, p-Ph of BAr_F), 7.18-7.14 (overlapping, 15H total, 10H, m-Ph, 5H, p-Ph), 6.85 (m, 10H, o-Ph), 5.12 (br, 2H, W-OH₂), 3.78 (s, 10H, CH₂Ph), 2.41 (br, free H_2 O). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz, 296 K): δ (ppm) 227.7 (CO), 221.7 (CO), 162.3 (q, ${}^{4}J_{CB} = 50$ Hz, *i*-Ph of BAr_F), 137.3 (*i*-Ph), 135.4 (s, *o*-Ph of BAr_F), 129.6 (*m*-Ph), 129.5 (qm, ${}^{2}J_{CF} = 30$ Hz, m-Ph of BAr_F), 128.9 (o-Ph), 128.2 (p-Ph), 125.2 (q, ${}^{1}J_{CF} = 272$ Hz, CF₃ of BAr_F), 118.1 (m, ${}^{3}J_{CF} = 4$ Hz, p-Ph of BAr_F), 115.3 (C_5Bz_5) , 32.6 (CH_2Ph) . ¹⁹F{¹H} NMR $(CD_2Cl_2, 282.4 \text{ MHz}, 296 \text{ K})$: δ (ppm) -62.8 (s, CF₃). ¹¹B NMR (CD₂Cl₂, 96.3 MHz, 296 K): δ (ppm) -6.6 (m). IR (KBr pellet): ν_{OH} 3677 and 3613 cm⁻¹ (w, br).

Solution NMR Studies. In order to obtain the relaxation matrixes²¹ for the exchange of phenyl rings in compound 3, twodimensional exchange spectra, 2D-EXSY, were acquired using the NOESY pulse sequence of the Bruker library over a reduced spectral width of 1500 Hz centered on the aromatic proton region. The mixing time was optimized to 500 ms, long enough to get good signal to noise but short enough to avoid relaxation effects. All 2D spectra were acquired as a $1k \times 64$ data array with 8 scans per increment. After zero filling to get the same digital resolution on both dimensions, the spectra were processed with a shifted square sine bell in both t1 and t2 domains. The exchange rate constants at 15, 17.5, 20, 25, and 30 °C were then calculated with the EXSYCALC program (Mestrelab Research, Santiago de Compostela, Spain) for a three-site exchange process. The volumes of diagonal and cross peaks of 2D-EXSY spectra needed for the calculations were measured using the SPARKY software (T. D. Goddard and S. G. Kneller, University of California at San Francisco). At each temperature the equilibrium magnetization of each site was also determined by integration of the diagonal peaks of a 2D-EXSY spectrum ran with a very short mixing time of 2 ms.

Computational Details. All calculations were performed using the Gaussian 03 software package,²² and the PBE0 functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including a 25% mixture of Hartree-Fock²³ exchange with DFT exchange correlation, given by the Perdew, Burke, and Ernzerhof functional (PBE).²⁴ The optimized geometries were obtained with a LanL2DZ basis set²⁵ augmented with an fpolarization function²⁶ for Mo and W and a standard $6-31G(d,p)^{27}$ for the remaining elements (basis b1). Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel et al.,28 following extensive searches of the potential energy surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition state and none for the minima. The transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profile. A natural population analysis (NPA)²⁹ and the resulting Wiberg indices¹⁹ were used to study the electronic structure and bonding of the optimized species. The electronic energies (E_{b1}) obtained were converted to standard enthalpies at 298.15 K ($H_{\rm h1}$) by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the PBE0/b1 level of theory.

Single point energy calculations were performed using a improved basis set (basis b2) and the geometries optimized at the PBE0/b1 level. Basis b2 consisted of a 3-21G basis set³⁰ with an added f polarization function²⁶ for Mo and standard 6-311++G(d,p)³¹ for the remaining elements (basis b1 was used for W). Solvent effects (CH₂Cl₂) were considered in the PBE0/b2//PBE0/b1 energy calculations using the polarizable continuum model (PCM) initially devised by Tomasi and co-workers³² as implemented in Gaussian 03.³³ The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level.

The enthalpy values presented along the text (H_{b2}^{soln}) were derived from the electronic energy values obtained at the PBE0/b2//PBE0/b1 level, including solvent effects (E_{b2}^{soln}) , according to the expression

$$H_{\rm b2}^{\rm soln} = E_{\rm b2}^{\rm soln} + H_{\rm b1} - E_{\rm b1}$$

X-ray Data Collection, Structure Solution, and Refinement. Suitable crystals of compounds 9 and 10 were selected and coated in FOMBLIN oil and mounted on a Bruker AXS-KAPPA APEX II diffractometer using graphite-monochromated Mo K α radiation (λ = 0.710 73 Å). A full sphere of data was collected at 150(2) K using ω scans of 0.5° per frame. Cell parameters were retrieved using Bruker APEX2 software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.³⁴ Structure solution and refinement were performed using direct methods with the programs SIR97³⁵ and SHELXS-97,³⁶ both included in the package of programs WINGX-Version 1.80.05.³⁷ Non-hydrogen atoms were refined anisotropically. All hydrogens were inserted in idealized positions and refined riding on the parent carbon atom. Torsion angles, mean square planes, and other geometrical parameters were calculated using SHELX.38 Illustrations of the molecular structures were made with ORTEP3.39 Details of the data collection and refinement are given in Table 3. Data for complexes 9 and 10 were deposited at the Cambridge Crystallographic Data Centre with references CCDC 837442 and 837443, respectively.

ASSOCIATED CONTENT

Supporting Information

Figure S1, giving the Eyring plot for benzyl exchange in 3, Figure S2, giving a representation of the optimized structure of intermediate A, tables giving atomic coordinates for all optimized species, and CIF files giving crystallographic data for complexes 9 and 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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