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Syntheses, Electrochemistry, and Bonding of Bis(cyclopentadienyl)molybdenum Alkyl Complexes. Molecular Structure of $Mo(\eta^5\text{-}C_5H_5)_2(C_4H_9)_2$. Thermochemistry of $Mo(\eta^5\text{-}C_5H_5)_2R_2$ and $Mo(\eta^5\text{-}C_5H_5)_2L$ ($R = CH_3, C_2H_5, C_4H_9$; L = Ethylene, Diphenylacetylene)

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Received April 30, 1990

$Mo(Cp)_2I_2$ ($Cp = \eta^5\text{-}C_5H_5$) reacts with lithium alkyls to afford the new complexes $Mo(Cp)_2R_2$ (R = Et, Bu) in reproducible yields. Reaction of $Mo(Cp)_2Me_2$ with 1 equiv of HX gives the complexes $Mo(Cp)_2XMe$ ($X = Cl, O_2CPh$). The mixed dialkyl $Mo(Cp)_2MeBu$ is prepared from $Mo(Cp)_2ClMe$ and LiBu, whereas EtMgBr reacts with $Mo(Cp)_2Me(O_2CPh)$ to give $Mo(Cp)_2BrMe$. Cyclic voltammetry studies on the dialkyls and halo alkyls show that they undergo one-electron oxidation. The ease of oxidation of these complexes decreases in the order $Me_2 > MeBu > Bu_2 > Et_2 > ClMe > BrMe$. The corresponding 17-electron cations are prepared by oxidation of $Mo(Cp)_2R_2$ and $Mo(Cp)_2XMe$ with the ferrocenium cation. The possible existence of agostic interactions in alkyl derivatives of $M(Cp)_2$ fragments (M = Ti, Zr, Mo) was investigated by extended Hückel molecular orbital calculations. These interactions do not appear to be favored in the 17-electron $Mo(Cp)_2Me_2^+$. The ease of oxidation of the dimethyl complex is attributed to a relatively high energy HOMO caused by the methyl groups acting as π-donors. A similar π-donor interaction also explains the relative order of oxidation potentials found for $Mo(Cp)_2XMe$ (X = Cl, Br). The structure of the complex $Mo(Cp)_2Bu_2$ was determined by X-ray diffraction. The crystals are monoclinic, space group $C2/m$, with $a = 2160.8$ (7) pm, $b = 786.3$ (3) pm, $c = 1955.2$ (8) pm, $\beta = 100.65$ (3)°, $V = 3264.7 \times 10^6$ pm^3, and $Z = 8$. The butyl ligands lie almost in the plane bisecting the angle defined by the ring normals, the C–Mo–C angle being 76.6 (2)°. Metal-carbon bond enthalpies in the complexes $Mo(Cp)_2R_2$ (R = Me, Et, Bu) and $Mo(Cp)_2L$ ($L = C_2H_4, C_2Ph_2$) were derived from reaction-solution calorimetry studies. The values for the dialkyl compounds, together with literature data, indicate that the differences $\bar{D}$(M–Me) – $\bar{D}$(M–higher alkyl) are nearly constant along the periodic table, in contrast with $\bar{D}$(M–H) – $\bar{D}$(M–alkyl) values, which are lower for more electropositive metals. The influence of these trends on the energetics of β-elimination and olefin insertion reactions is discussed. The Mo–C_2H_4 bond dissociation enthalpy is about 60 kJ mol^{-1} lower than D(Mo–C_2Ph_2).

Introduction

The understanding of transition-metal–carbon bonds in their structural, energetic, and reactivity aspects plays a central role in organotransition-metal chemistry. In this respect, the metallocene derivatives $M(Cp)_2R_2$ (M = Mo, W; $Cp = \eta^5\text{-}C_5H_5$; R = H, Me, Ph) have proved to be excellent models in a number of studies. For example, the easy preparation of thermally and kinetically stable complexes bearing the otherwise rare *cis*-MR_2, *cis*-MH_2, and *cis*-M(R)H fragments has allowed very important and detailed studies on C–H activation,[1] olefin and acetylene insertion into M–H bonds,[2] thermally and photochemically induced β-elimination,[3] thermochemical M–C and M–H bond enthalpy determination,[4] and selective α-H abstraction.[5] In this paper we present results closely pertaining to the last two topics, which are of particular interest to us.

The preparation and characterization of the new $Mo(Cp)_2R_2$ complexes (R = Et, Bu) enabled their thermochemical study and a discussion of the effect of the alkyl chain length on the molybdenum–carbon bond enthalpies. Despite the importance of this type of data to understand the energetics of elementary steps such as β-elimination and C–H activation of alkanes, there are very few families of organometallic molecules for which thermochemical information is available.[6] The scarcity of experimental values of metal–alkene and metal–alkyne bond enthalpies is even more noteworthy, particularly for complexes of early and middle transition elements.[7] We therefore decided to determine the molybdenum–carbon bond enthalpies in the complexes $Mo(Cp)_2(C_2H_4)$ and $Mo(Cp)_2(C_2Ph_2)$.

As observed for the dimethyl complex $Mo(Cp)_2Me_2$,[8,9]

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the higher alkyl compounds $Mo(Cp)_2Et_2$ and $Mo(Cp)_2Bu_2$ are readily oxidized to the stable 17-electron cations $Mo(Cp)_2R_2^+$. This prompted the electrochemical study of these and the related $Mo(Cp)_2XMe$ (X = Me, Bu, Cl, Br) molecules. The results parallel those reported by Asaro et al. for the tungsten analogues.[10] The effect of the alkyl substituent on the oxidation potentials of the dialkyls, namely $Mo(Cp)_2Me_2$ is easier to oxidize than $Mo(Cp)_2Et_2$ and $Mo(Cp)_2Bu_2$, is counterinductive. This was explained by Asaro et al. for the tungsten analogues on the basis of a three-electron agostic stabilization of the oxidized species.[10] However, in light of the results of the molecular orbital study described in the present paper, an alternative interpretation is advanced. Parts of this work have been previously communicated.[11]

Results and Discussion

Syntheses. It has long been established that β-hydrogen elimination from alkyl ligands is a facile reaction that hampers the preparation of higher homologues of many transition-metal alkyl complexes. At the outset of this work the only β-hydrogen-containing derivatives of the $Mo(Cp)_2$ moiety were $Mo(Cp)_2(CH_2)_4$,[12] $Mo(Cp)_2Et(PR_3)^+$, and $Mo(Cp)_2ClEt$.[8] The last species is an expected intermediate in the formation of $Mo(Cp)_2Et_2$ from $Mo(Cp)_2Cl_2$ and an alkylating agent, e.g. $AlEt_3$ or EtMgBr. However, as Benfield and Green have shown, it yields β-elimination products such as $Mo(Cp)_2H(C_2H_4)^+$, in the presence of $(AlEtCl_2)_2$ or $TlPF_6$, and $Mo(Cp)_2(C_2H_4)$ in the presence of PhLi.[8]

In agreement with the above results, we found that $Mo(Cp)_2Cl_2$ reacts with $AlEt_3$ in toluene, to give $Mo(Cp)_2(C_2H_4)$, but when diethyl ether is used as solvent, $Mo(Cp)_2Et_2$ is formed, albeit in small and irreproducible yields. Again, no $Mo(Cp)_2Bu_2$ is formed in similar reactions with $AlBu_3$ either in toluene or diethyl ether. The use of $LiAlBu_4$, however, gives a small yield of $Mo(Cp)_2Bu_2$, and this led us to try simple lithium alkyls.

When the dichloride or dibromide derivatives $Mo(Cp)_2X_2$ (X = Cl, Br) are used, the results are as found for the aluminum and Grignard reagents. On the other hand, use of $Mo(Cp)_2I_2$ and LiR (R = Et, Bu) leads to the reproducible formation of $Mo(Cp)_2R_2$ (R = Et, Bu) in modest yields. Both compounds can be handled in air for short periods of time and are rather thermally stable, decomposing at ca. 120 °C. $Mo(Cp)_2Et_2$ is readily sublimable at 60 °C and 0.1 Pa. The analytical and spectroscopic data (see Experimental Section) entirely agree with the $Mo(Cp)_2R_2$ (R = Et, Bu) formulation. A crystal structure determination was done on $Mo(Cp)_2Bu_2$ (see below).

The previous observations indicate that the difficulty of preparing β-hydrogen-containing dialkyls of the $Mo(Cp)_2$ moiety does not lie in their intrinsic instability (meant in a global thermodynamic and kinetic sense) but rather in the kinetic instability of some reaction intermediate toward β-hydrogen elimination. In our system this situation will arise when the intermediate $Mo(Cp)_2XR$ interacts with the Lewis acid of the alkylating agent M′ (M′ = Al, Mg, Li), through a Mo- - -X- - -M′ bridge that leads primarily to Mo–X bond breaking, therefore facilitating β-hydrogen elimination from the adjacent R group. Of course, the nature of this interaction is not easily predictable, depending on M′, X, and solvents. Only a thorough variation of experimental conditions will eventually lead to the desired results.

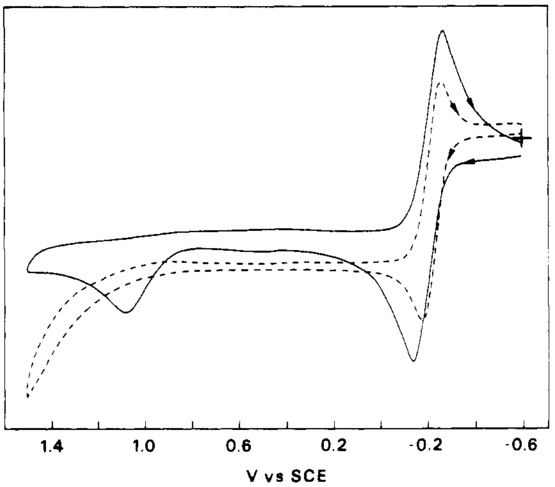

Figure 1. Cyclic voltammograms of $Mo(Cp)_2Et_2$, 0.1 M $[Bu_4N]PF_6$ in CH_2Cl_2 (solid line) and in MeCN (dotted line). The sweep rate was 100 mV/s.

Table I. Electrochemical Data[a]

complex	ΔE_p/mV		$^1/_2(E_a + E_c)$/mV		i_a/i_c	
	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2
$Mo(Cp)_2Me_2$	90	90	−275	−270	0.98	1.00
$Mo(Cp)_2Et_2$	90	135	−215	−207	1.03	0.98
$Mo(Cp)_2Bu_2$	80	90	−220	−215	0.97	1.00
$Mo(Cp)_2$-BuMe	80	80	−270	−240	0.98	0.98
$Mo(Cp)_2ClMe$	70	75	55	120	1.00	1.00
$Mo(Cp)_2$-BrMe[b]		90		155		0.79

[a] Cyclic voltammetry was performed at room temperature on solutions of the complex (10^{-3} M) and $[Bu_4N]PF_6$ (0.10 M; the supporting electrolyte) at a scan rate of 100 mV s^{-1}. Potentials are referenced to a calomel electrode containing a saturated potassium chloride solution. [b] Reacts instantaneously in the electrochemical cell when the solvent is acetonitrile.

The advantage of lithium alkyls for alkylation reactions in this system was again observed in the attempted preparations of the mixed dialkyls $Mo(Cp)_2MeR$ (R = Et, Bu). In a first step $Mo(Cp)_2XMe$ compounds (X = Cl, O_2CPh) were prepared from $Mo(Cp)_2Me_2$ and HX and characterized. Further reaction of the benzoate derivative with EtMgBr led, quite unexpectedly, to $Mo(Cp)_2BrMe$. The $Mo(Cp)_2XMe$ (X = Cl, Br) complexes reacted with EtMgBr to give an as yet uncharacterized thermally labile product. On the other hand, $Mo(Cp)_2ClMe$ reacts cleanly with LiBu to give $Mo(Cp)_2BuMe$.

As observed for the dimethyl analogue,[8,9] the complexes $Mo(Cp)_2R_2$ (R = Et, Bu) and $Mo(Cp)_2XMe$ (X = Cl, Bu) are quantitatively oxidized by $Fe(Cp)_2(PF_6)$ to give the corresponding 17-electron cations $[Mo(Cp)_2XMe]^+$. These are stable in air and in acetonitrile solutions but slowly decompose in acetone and exhibit an ESR signal in the expected range.

Electrochemistry. The cyclic voltammograms of $Mo(Cp)_2R_2$ (R = Me, Et, Bu) and $Mo(Cp)_2XMe$ (X = Bu, Cl, Br) compounds in acetonitrile and dichloromethane, within the solvent limits (ca. −1.5 to +1.6 V), exhibited a

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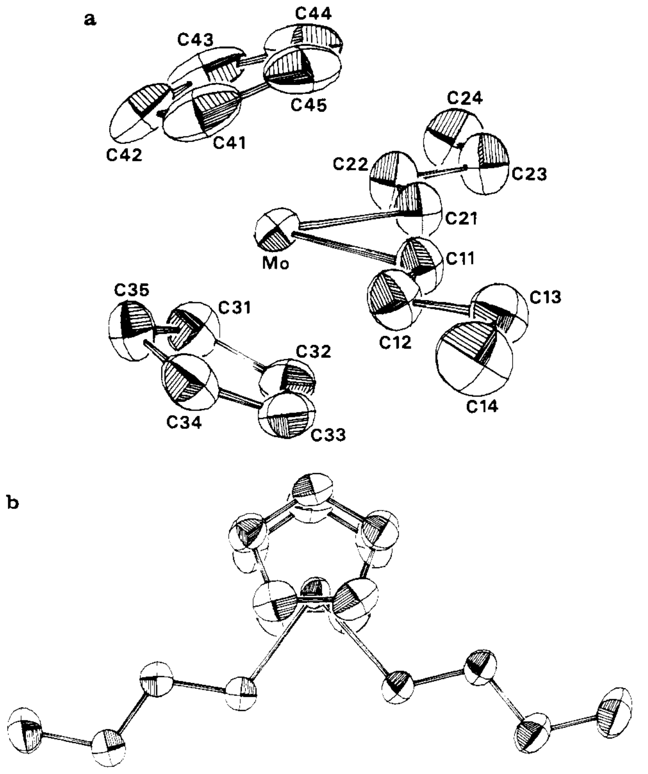

Figure 2. Molecular structure of $\mathrm{Mo(Cp)_2Bu_2}$ with 50% thermal ellipsoids: (a) side view; (b) projection onto the C(11), Mo, C(21) plane.

chemically quasi-reversible one-electron oxidation at scan rates between 20 and 1000 mV/s. The cyclic voltammogram of $\mathrm{Mo(Cp)_2Et_2}$ (Figure 1) exemplifies the typical behavior of the complexes.

A linear relation was obtained by plotting i_a against the square root of the scan speed in the range of the above potentials, as expected for a diffusion-controlled electrode process. The average of the anodic and cathodic peak potentials is independent of the scan speed, and the separation of the waves, ΔE_p, is normally close to 80 mV (Table I). The oxidation was slightly more reversible in acetonitrile than in dichloromethane. For $\mathrm{Mo(Cp)_2Et_2}$, however, ΔE_p = 135 mV in dichloromethane. These observations suggest a possible stabilization of the oxidized form by acetonitrile. Furthermore, when the experiments were carried out in dichloromethane, in addition to the first oxidation, a second irreversible wave was found at 1.10, 1.05, 1.02, and 1.05 V, respectively, for $\mathrm{Mo(Cp)_2Me_2}$, $\mathrm{Mo(Cp)_2Et_2}$, $\mathrm{Mo(Cp)_2Bu_2}$, and $\mathrm{Mo(Cp)_2BuMe}$.

The one-electron character of the oxidation was confirmed by controlled-potential coulometry. Oxidation of the bulk acetonitrile solutions of the complexes at potentials 200 mV more positive than the corresponding cyclic voltammetry oxidation peak involved an average 0.9 electron.

Table I shows that the oxidation potentials of the complexes are in a different order from what should be expected on the basis of the inductive effects of the alkyl groups. These results parallel those obtained by Asaro et al.[10] for the tungstenocene analogues. Replacement of Et by Me in $\mathrm{M(Cp)_2R_2}$ decreases the oxidation potentials by similar amounts for M = Mo and W (60 mV for M = Mo and 65 mV for M = W in acetonitrile).

As expected, the half-wave oxidation potentials ($E_{\mathrm{p}/2}$) of the mixed alkyl halide derivatives $\mathrm{Mo(Cp)_2XMe}$ (X = Cl, Br) (Table I) lie between that observed for the dimethyl complex and those measured for $\mathrm{Mo(Cp)_2Cl_2}$ and $\mathrm{Mo(Cp)_2Br_2}$ in the same solvent, 0.51 and 0.54 V, respectively.[13]

Table II. Fractional Atomic Coordinates (×10⁴) for $\mathrm{Mo(Cp)_2Bu_2}$

	x	*y*	*z*
Mo	1286	-1381	1321
C(11)	408 (1)	-2899 (3)	886 (1)
C(12)	119 (1)	-3951 (3)	1402 (1)
C(13)	-433 (1)	-5064 (4)	1073 (2)
C(14)	-741 (2)	-5998 (5)	1593 (2)
C(21)	1100 (1)	-715 (3)	169 (1)
C(22)	1562 (1)	515 (3)	-65 (1)
C(23)	1455 (2)	870 (4)	-837 (1)
C(24)	1917 (2)	2122 (5)	-1040 (2)
C(31)	1412 (2)	1432 (3)	1636 (2)
C(32)	801 (1)	1308 (3)	1242 (2)
C(33)	445 (1)	228 (3)	1584 (2)
C(34)	823 (1)	-349 (4)	2204 (1)
C(35)	1420 (1)	421 (3)	2237 (1)
C(41)	1761 (2)	-3723 (4)	1887 (2)
C(42)	2189 (1)	-2340 (5)	1974 (2)
C(43)	2330 (1)	-1923 (5)	1317 (2)
C(44)	2003 (2)	-3048 (4)	837 (2)
C(45)	1653 (2)	-4134 (4)	1182 (2)

Table III. Bond Lengths (pm) and Bond Angles (deg) for $\mathrm{Mo(Cp)_2Bu_2}$

C(11)-Mo	226.8 (4)	C(21)-Mo	227.2 (4)
C(31)-Mo	229.7 (4)	C(32)-Mo	235.0 (4)
C(33)-Mo	234.7 (4)	C(34)-Mo	229.7 (4)
C(35)-Mo	225.9 (4)	C(41)-Mo	229.0 (4)
C(42)-Mo	225.5 (4)	C(43)-Mo	229.7 (4)
C(44)-Mo	235.6 (4)	C(45)-Mo	233.7 (4)
C(12)-C(11)	152.5 (5)	C(13)-C(12)	152.1 (5)
C(14)-C(13)	150.5 (6)	C(22)-C(21)	152.0 (5)
C(23)-C(22)	151.0 (5)	C(24)-C(23)	150.7 (5)
C(32)-C(31)	140.4 (5)	C(35)-C(31)	141.6 (4)
C(33)-C(32)	139.6 (5)	C(34)-C(33)	140.5 (4)
C(35)-C(34)	141.6 (4)	C(42)-C(41)	141.6 (5)
C(45)-C(41)	139.2 (5)	C(43)-C(42)	141.3 (5)
C(44-C(43)	138.4 (5)	C(45)-C(44)	139.3 (5)
C(21)-Mo-C(11)	76.6 (2)	C(31)-Mo-C(11)	131.0 (1)
C(31)-Mo-C(21)	92.0 (2)	C(32)-Mo-C(11)	96.7 (2)
C(32)-Mo-C(21)	74.5 (2)	C(32)-Mo-C(31)	35.1 (1)
C(33)-Mo-C(11)	74.8 (2)	C(33)-Mo-C(21)	95.2 (2)
C(33)-Mo-C(31)	58.8 (2)	C(33)-Mo-C(32)	34.6 (1)
C(34)-Mo-C(11)	91.0 (2)	C(34)-Mo-C(21)	129.9 (2)
C(34)-Mo-C(31)	60.4 (2)	C(34)-Mo-C(32)	58.8 (2)
C(34)-Mo-C(33)	35.2 (1)	C(35)-Mo-C(11)	127.1 (2)
C(35)-Mo-C(21)	127.9 (2)	C(35)-Mo-C(31)	36.2 (1)
C(35)-Mo-C(32)	58.6 (2)	C(35)-Mo-C(33)	58.7 (2)
C(35)-Mo-C(34)	36.2 (1)	C(41)-Mo-C(11)	91.6 (2)
C(41)-Mo-C(21)	130.2 (1)	C(41)-Mo-C(31)	128.5 (2)
C(41)-Mo-C(32)	155.3 (1)	C(41)-Mo-C(33)	128.5 (2)
C(41)-Mo-C(34)	98.0 (2)	C(41)-Mo-C(35)	98.0 (2)
C(42)-Mo-C(11)	127.7 (2)	C(42)-Mo-C(21)	127.9 (2)
C(42)-Mo-C(31)	97.0 (2)	C(42)-Mo-C(32)	131.8 (1)
C(42)-Mo-C(33)	132.8 (1)	C(42)-Mo-C(34)	98.2 (2)
C(42)-Mo-C(35)	77.8 (2)	C(42)-Mo-C(41)	36.3 (1)

Crystallography. The structure of $\mathrm{Mo(Cp)_2Bu_2}$ is shown in Figure 2a, along with the atom-numbering scheme. Final atomic positional parameters for the nonhydrogen atoms are given in Table II. Bond lengths and angles are given in Table III.

The metal is coordinated to two η^5-cyclopentadienyl rings and two butyl ligands, in a distorted-tetrahedral environment, with an angle between ring normals of 135.2 (1)°. The two Cp rings are in an eclipsed conformation, as seen more clearly in Figure 2b.

An interesting feature of this structure is the position of the two butyl ligands, which lie almost in the plane

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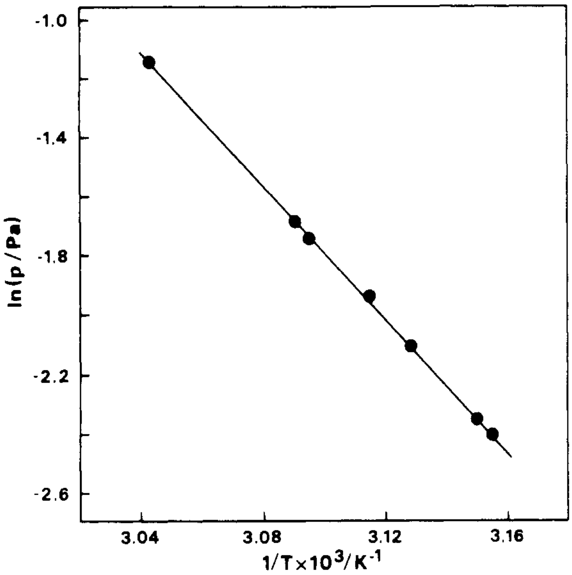

Figure 3. Vapor pressure of $Mo(Cp)_2Et_2$.

bisecting the angle defined by the ring normals. The maximum deviation from this plane is 7 pm for C(13).

The Mo–C bond lengths of 227.1 (4) and 226.8 (4) pm are comparable to 226.7 (12) and 227.0 (16) pm, observed in $Mo(Cp_2)(CH_2)_4$,[12] 228.4 (10) pm in $Mo(Cp_2)ClEt$,[14a] 226.9 (7) pm in $[Mo(Cp)_2(PPh_3)Me][PF_6]$,[14b] and 230.6 (3) pm in $Mo(Cp)_2(CHMeCN)(SPh)$.[14c] However, other complexes without Cp ligands have shorter Mo–C bond lengths. Typical values are 221 and 219 pm in $Mo(bpy)(O)_2Et_2$,[15a] 224 pm in $Mo(bpy)(O)_2(CH_2CMe_3)_2$,[15b] and 216 and 217 pm in $Mo(NMe_2)_4Et_2$.[15c]

The angle Bu–Mo–Bu (76.6 (2)°) is comparable to the C–Mo–C angle in the complex $Mo(Cp)_2(CH_2)_4$[12] (74.9 (5)°), which indicates a strain-free metallacycle (the equivalent angles in four-membered metallacycles are ca. 60°).[16] It is also close to the value of 78° predicted by extended Hückel molecular orbital calculations for d^2 metallocene complexes.[17]

The butyl ligands have the expected geometries with C–C bond lengths in the range 150.5–152.5 pm.

Thermochemistry. The enthalpy of sublimation of $Mo(Cp)_2Et_2$ was derived from vapor pressure–temperature data obtained with a Knudsen cell.[18,19] The vapor pressures (p/Pa) were calculated through eqs 1 and 2,[18-20]

$$p = \frac{m}{At}\left(\frac{2\pi RT}{M}\right)^{1/2}\frac{3l + 8r}{8r}\,\frac{1}{1 + 0.24r/\lambda} \qquad (1)$$

$$\lambda = kT/2^{1/2}\pi\sigma^2 p \qquad (2)$$

where m/g is the mass loss over time t/s, A/cm² is the area of the effusion hole, T/K is the temperature, r/cm is the hole radius, l/cm is the thickness of the foil where the hole was drilled, λ/cm is the mean free path, k and R are the Boltzmann and gas constants, respectively, M/g mol⁻¹ is the molecular weight of the gaseous species, and σ is its collision diameter. A value σ = 660 pm was deduced from projections of the estimated molecular structure of the complex on the x, y, z planes. Similar bond lengths and angles were assumed for $Mo(Cp)_2Et_2$ and $Mo(Cp)_2Bu_2$; van der Waals radii were accounted for.[21] A change of ca. 20% in the collision diameter affects the value of the enthalpy of sublimation by about 2%.

The vapor pressure–temperature data (Figure 3) were adjusted to the Clausius–Clapeyron equation by the least-squares method, yielding the linear relation (3), from which $\Delta H^\circ_s[Mo(Cp)_2Et_2] = 93.6 \pm 1.8$ kJ mol⁻¹ was derived (temperature range 317.05–328.65 K). It is assumed that

$$\ln\,(p/\mathrm{Pa}) = (33.093 \pm 0.255) - (11\,252 \pm 82)/T \qquad (3)$$

the correction to 298 K is negligible. The uncertainty intervals presented include a Student factor for the 95% confidence level (t = 2.571).

Calorimetric measurements on reactions 4–7 (the letter c denotes the crystalline form) were used to derive the standard enthalpies of formation of the reactant complexes. The products $Mo(Cp)_2Cl_2$ and $Mo(Cp)_2I_2$ were

$$Mo(Cp)_2Et_2(c) + 2HCl(soln) \rightarrow Mo(Cp)_2Cl_2(c) + 1.6C_2H_6(soln) + 0.4C_2H_6(g) \qquad (4)$$

$$Mo(Cp)_2Bu_2(c) + 2HCl(soln) \rightarrow Mo(Cp)_2Cl_2(c) + 1.99C_4H_{10}(soln) + 0.01C_4H_{10}(g) \qquad (5)$$

$$Mo(Cp)_2(C_2H_4)(c) + I_2(soln) \rightarrow Mo(Cp)_2I_2(c) + 0.8C_2H_4(soln) + 0.2C_2H_4(g) \qquad (6)$$

$$Mo(Cp)_2(C_2Ph_2)(c) + I_2(soln) \rightarrow Mo(Cp)_2I_2(c) + C_2Ph_2(soln) \qquad (7)$$

confirmed by IR spectroscopy, and the amounts of ethylene, ethane, and butane present in the gas and liquid phases were evaluated by GC analysis (see Experimental Section). The calorimetric solvent was a 1.34 mol dm⁻³ solution of anhydrous HCl in isopropyl ether for reactions 4 and 5 and solutions of I_2 in toluene for reactions 6 and 7. Iodine–complex molar ratios varied from ca. 6 to 11 and from 4 to 19, respectively, for reactions 6 and 7.

The determination of the enthalpy of formation of the 1.34 mol dm⁻³ solution of HCl in isopropyl ether (d^{20} = 0.748 g cm⁻³) was based on reactions of this mixture with aqueous NaOH (4.8 mol dm⁻³) and cyclohexylamine (reactions 8 and 9). As a test for the internal consistency

$$1{:}5.11\ HCl\text{–}C_6H_{14}O(soln) + 1{:}11.4\ NaOH\text{–}H_2O(aq) \rightarrow 12.4H_2O(soln) + NaCl(soln) + 5.11C_6H_{14}O(soln) \qquad (8)$$

$$1{:}5.11\ HCl\text{–}C_6H_{14}O(soln) + C_6H_{11}NH_2(l) \rightarrow C_6H_{11}NH_3Cl(c) + 5.11C_6H_{14}O(soln) \qquad (9)$$

of our data, reaction 10, previously studied in aqueous solution,[22] was repeated in the HCl/isopropyl ether mixture. The final state of reaction 10 was determined by IR and GC analysis.

$$Mo(Cp)_2(CH_3)_2(c) + 2HCl(soln) \rightarrow Mo(Cp)_2Cl_2(c) + 1.1CH_4(soln) + 0.9CH_4(g) \qquad (10)$$

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(22) See ref 4 and references cited therein.

Table IV. Auxiliary Thermochemical Data (kJ mol^{-1})[a]

molecule	$\Delta H°_f$	$\Delta H°_s$
$Mo(Cp)_2Cl_2(c)$	-95.8 ± 2.5[b]	(100.4 ± 4.2)[b]
$Mo(Cp)_2I_2(c)$	69.8 ± 7.8[b]	(100.4 ± 4.2)[b]
$Mo(Cp)_2Me_2(c)$	262.4 ± 4.0[b]	70.4 ± 4.2[b]
$Mo(Cp)_2H_2(c)$	210.3 ± 5.7[b]	81.4 ± 1.0[b]
$CH_4(g)$	-74.5 ± 0.4[c]	
$C_2H_4(g)$	52.2 ± 1.2[c]	
$C_2H_6(g)$	-84.0 ± 0.2[c]	
$C_4H_{10}(g)$	-126.5 ± 0.4[c]	
$C_2Ph_2(c)$	312.4 ± 1.0[c]	99.9 ± 1.5[d]
$C_6H_{13}N(l)$	-147.7 ± 1.3[c]	
$C_6H_{14}NCl(c)$	-408.2 ± 1.4[c]	
$H_2O(l)$	-285.830[e]	
$NaCl(c)$	-411.153[e]	
1:11.4 $NaOH-H_2O(aq)$	-469.905[e]	
$H(g)$	217.965[e]	
$Cl(g)$	121.679[e]	
$Me(g)$	146.9 ± 0.6[f]	
$Et(g)$	119 ± 4[f]	
$Bu(g)$	(74 ± 8)[f]	

[a] Values in parentheses are estimates. [b] Reference 22. [c] References 23 and 24. [d] Reference 19. [e] Reference 25. [f] Values selected in ref 26.

Table V. Thermochemical Results (kJ mol^{-1})

molecule	$-\Delta H_r$	ΔH_{d2}[a]
$Mo(Cp)_2Me_2$	200.6 ± 3.9	(-4 ± 2)
$Mo(Cp)_2Et_2$	194.8 ± 1.4	(-11 ± 2)
$Mo(Cp)_2Bu_2$	204.1 ± 3.5	(-18 ± 2)
$Mo(Cp)_2(C_2H_4)$	186.0 ± 2.1	-8.8 ± 0.5[b]
$Mo(Cp)_2(C_2Ph_2)$	129.4 ± 1.3	15.68 ± 0.84

[a] Values in parentheses are estimates based on solubility data in: Wilhelm, E.; Batino, R. *Chem. Rev.* **1973**, *73*, 1. Cone, J.; Smith, L. E. S.; Van Hook, W. A. *J. Chem. Thermodyn.* **1979**, *11*, 277. For methane and ethane the enthalpies of solution in a number of solvents, including aliphatic and aromatic hydrocarbons, acetone, alcohols, and tetrahydrofuran, vary from ca. -2.3 to -5.2 kJ mol^{-1} and from -8.6 to -12.6 kJ mol^{-1}, respectively. Data from the above references show that, for aliphatic hydrocarbon gases, excellent linear relations are obtained if the enthalpies of vaporization are plotted against enthalpies of solution in a given solvent. The value quoted for butane was based on this correlation and on ΔH_{d2} estimated for methane and ethane. [b] See the first reference in footnote *a*.

Table VI. Enthalpies of Formation (kJ mol^{-1})[a]

molecule	$\Delta H°_f(c)$	$\Delta H°_s$	$\Delta H°_f(g)$
$Mo(Cp)_2Me_2$	238.3 ± 5.4	70.4 ± 4.2	308.7 ± 6.8
$Mo(Cp)_2Et_2$	200.3 ± 4.6	93.6 ± 1.8	293.9 ± 4.9
$Mo(Cp)_2Bu_2$	106.4 ± 6.1	(103 ± 10)	209.4 ± 11.7
$Mo(Cp)_2(C_2H_4)$	285.0 ± 8.2	(77 ± 10)	362.0 ± 12.9
$Mo(Cp)_2(C_2Ph_2)$	511.4 ± 8.0	(150 ± 20)	661 ± 22

[a] Values in parentheses are estimates.

Auxiliary values used in evaluating the thermochemical results were quoted from the literature[4,23-26] and are collected in Table IV.

The thermochemical results for reactions 4–7 and 10 are summarized in Table V. All reaction and solution enthalpies presented are mean values of five independent experiments at 298 K. The uncertainties reported are twice the standard deviation of the mean for each case. ΔH_r refers to the enthalpy of reactions 4–7 or 10. ΔH_{d1}, the enthalpy of solution of the dichloride or diiodide complexes in the HCl–isopropyl ether or I_2–toluene solutions, respectively, was taken as zero, since a complete precipitation of these complexes was observed (endothermic heat effects measured by breaking ampules of $Mo(Cp)_2Cl_2$ and $Mo(Cp)_2I_2$ in the solutions were comparable to those observed with empty ampules). ΔH_{d2} is the enthalpy of solution of the ligand in mixtures of HCl/isopropyl ether or I_2/toluene containing stoichiometric amounts (in suspension) of $Mo(Cp)_2Cl_2$ or $Mo(Cp)_2I_2$, respectively. $\Delta H_{d3} = -0.13 \pm 0.04$ kJ mol^{-1}, which gives the enthalpy change associated with the dilution of the acid solution, was determined by breaking ampules containing pure isopropyl ether in the 1.34 mol dm^{-3} solution of HCl in isopropyl ether. The enthalpy of solution of iodine in toluene was taken as $\Delta H_{d4} = 15.92 \pm 0.16$ kJ mol^{-1}.[27]

Calorimetric measurements on reaction 8 gave $\Delta H_r(8) = -81.34 \pm 0.39$ kJ mol^{-1}. Lower values were obtained if the ampules were not completely filled with the acid solution. This may be attributed to the fact that gaseous HCl inside the ampules escapes from the calorimetric solvent before it reacts with NaOH. Auxiliary measurements necessary to derive the enthalpy of formation of the 1.34 mol dm^{-3} solution of HCl in isopropyl ether were the enthalpy of the solution of H_2O in 4.8 mol dm^{-3} aqueous NaOH ($\Delta H_{d5} = -0.33 \pm 0.04$ kJ mol^{-1}), the enthalpy of the solution of NaCl in 4.8 mol dm^{-3} aqueous NaOH ($\Delta H_{d6} = -0.76 \pm 0.09$ kJ mol^{-1}), and the enthalpy of the solution of $C_6H_{14}O$ in 4.8 mol dm^{-3} aqueous NaOH containing stoichiometric amounts of NaCl ($\Delta H_{d7} = -1.27 \pm 0.06$ kJ mol^{-1}). These values lead to $\Delta H°_f$ (1:5.11 $HCl-C_6H_{14}O$(soln)) $= -144.1 \pm 0.7$ kJ mol^{-1}, calculated from eq 11.

$$\Delta H°_f(1{:}5.11\ HCl\text{-}C_6H_{14}O(soln)) = -\Delta H_r(8) + 12.4\Delta H_{d5} + \Delta H_{d6} + 5.11\Delta H_{d7} + \Delta H°_f(NaCl(c)) + \Delta H°_f(H_2O(l)) - \Delta H°_f(1{:}11.4\ NaOH\text{-}H_2O) \quad (11)$$

The reaction of cyclohexylamine with the HCl–isopropyl ether solution (reaction 9) gave $\Delta H_r(9) = -124.8 \pm 1.5$ kJ mol^{-1}, leading to $\Delta H°_f$(1:5.11 $HCl-C_6H_{14}O$(soln)) $= -136.4 \pm 2.4$ kJ mol^{-1}. This value is 7.7 kJ mol^{-1} higher than the one derived from reaction 8. Although the discrepancy is not serious, it is difficult to decide for any of these results. The reaction with cyclohexylamine is apparently clean, but the formation of a precipitate may have some small effect on $\Delta H_r(9)$. On the other hand, reactions of aniline and triethylamine with the same HCl mixture gave irreproducible results. With all this in mind we decided to use the former value for $\Delta H°_f$(1:5.11 $HCl-C_6H_{14}O$ (soln)), -144.1 ± 0.7 kJ mol^{-1}.

The standard enthalpies of formation of the crystalline complexes (Table VI) were calculated from eqs 12 and 13 by using the data in Tables IV and V (x is the number of moles of ligand in solution; see reactions 4–7 and 10). It

$$\Delta H°_f(Mo(Cp)_2R_2(c)) = -\Delta H_r + x\Delta H_{d2} + 10.22\Delta H_{d3} + 2\Delta H°_f(RH(g)) + \Delta H°_f(Mo(Cp)_2Cl_2(c)) - 2\Delta H°_f(1{:}5.11\ HCl\text{-}C_6H_{14}O(soln)) \quad (12)$$

$$\Delta H°_f(Mo(Cp)_2L(c)) = -\Delta H_r + x\Delta H_{d2} - \Delta H_{d4} + \Delta H°_f(L(g/c)) + \Delta H°_f(Mo(Cp)_2I_2(c)) \quad (13)$$

is noted that the above inconsistency in $\Delta H°_f$(1:5.11 $HCl-C_6H_{14}O$(soln)), 7.7 kJ mol^{-1}, may affect the accuracy of the enthalpies of formation of the dialkyl complexes by ca. 16 kJ mol^{-1}. The accuracy obtained for $\Delta H°_f$(Mo-

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Table VII. Bond Enthalpy Data (kJ mol^{-1})

molecule	E(M–L)[a]	$D/\bar{D}$(M–L)[b]	ER_1[c]	ER_3[c]	ER_L[d]
$Mo(Cp)_2H_2$[e]	257 ± 8	257 ± 8	–16	–82	0
$Mo(Cp)_2Me_2$[f]	236 ± 8	177 ± 8	–51	–82	–59
	(225 ± 8)	(166 ± 8)	–51	–82	–59
$Mo(Cp)_2Et_2$	218 ± 9	156 ± 9	–51	–82	–62
$Mo(Cp)_2Bu_2$	218 ± 12	154 ± 12	–51	–82	–64
$Mo(Cp)_2(C_2H_4)$		59 ± 20	–57	–82	
$Mo(Cp)_2(C_2Ph_2)$	152 ± 14[g]	120 ± 27	–30	–82	–184

[a] Values not affected by $(ER_3 - ER_1)/2$ but including ER_L (see text). If Laidler terms[30] are used, E(Mo–Me) = 153 kJ mol^{-1}, E(Mo–Et) = 146 kJ mol^{-1}, and E(Mo–Bu) = 146 kJ mol^{-1}. [b] Values not affected by $ER_3/2$. Data for ethylene and diphenylacetylene complexes are bond dissociation enthalpies, whereas those for the remaining molecules are *mean* bond dissociation enthalpies. [c] Values obtained from curves in ref 28. It was assumed that the Cp–Mo–Cp angles (135°) were similar in the dimethyl, diethyl, and dibutyl complexes. For $Mo(Cp)_2(C_2H_4)$ and $Mo(Cp)_2(C_2Ph_2)$ the Cp–M–Cp angles were taken as 134° (estimated) and 140.3°,[31] respectively. [d] Estimated by the MNDO method.[29] [e] Reference 4. [f] Values in parentheses from ref 4. [g] Calculated on the basis of two Mo–C bonds.

$(Cp)_2Me_2(c))$ is probably no better than 20 kJ mol^{-1}, as indicated by the comparison between the early value from this laboratory (262.4 ± 4.0 kJ mol^{-1}, Table IV) and the value in Table VI, 238.3 ± 5.4 kJ mol^{-1} (see discussion below). Also included in Table VI are the enthalpies of sublimation and the enthalpies of formation of the gaseous complexes at 298 K.

Bond enthalpy terms, E(M–L), bond dissociation enthalpies, D(M–L), and mean bond dissociation enthalpies, $\bar{D}$(M–L), in the complexes studied are presented in Table VII, which also includes earlier data obtained in our laboratory for Mo–H and Mo–Me bonds.[22] These values were calculated from eqs 14 and 15. The asterisk indicates a

$$E(\text{Mo–L}) = E(\text{Mo–Cl}) + (n/2)\Delta H^\circ_f(\text{L}^*(\text{g})) - \Delta H^\circ_f(\text{Cl}(\text{g})) - [\Delta H^\circ_f(\text{Mo}(\text{Cp})_2\text{L}_n(\text{g})) - \Delta H^\circ_f(\text{Mo}(\text{Cp})_2\text{Cl}_2(\text{g}))]/2 + (\text{ER}_3 - \text{ER}_1)/2 \quad (14)$$

$$D(\text{Mo–L}) = E(\text{Mo–Cl}) + (n/2)\Delta H^\circ_f(\text{L}(\text{g})) - \Delta H^\circ_f(\text{Cl}(\text{g})) - [\Delta H^\circ_f(\text{Mo}(\text{Cp})_2\text{L}_n(\text{g})) - \Delta H^\circ_f(\text{Mo}(\text{Cp})_2\text{Cl}_2(\text{g}))]/2 + \text{ER}_3/2 \quad (15)$$

nonreorganized fragment, i.e. a fragment retaining the geometry of the initial complex. ER_1 and ER_3 are the reorganization energies of the $Mo(Cp)_2$ moieties from the complex $Mo(Cp)_2L_n$ and from the "reference" molecule $Mo(Cp)_2Cl_2$, respectively. E(Mo–Cl) = 303.8 ± 7.1 kJ mol^{-1} is the bond enthalpy term in the dichloride complex, which was transferred from $MoCl_6$.[4]

The E value shown in Table VII for the diphenylacetylene complex was calculated on the basis of two Mo–C σ bonds by making $n = 1$ in eq 14. Since metal–carbon mean bond dissociation enthalpies, $\bar{D}$(M–C), are clearly meaningless parameters in this case, $D(Mo–C_2Ph_2) = 2\bar{D}$(Mo–C) is reported in Table VII. The same applies to the ethylene complex.

The reorganization energies ER_1 and ER_3 (Table VII) were estimated from a curve relating the total energy of the fragment $Mo(Cp)_2$ with the angle Cp–Mo–Cp.[28] As this curve relies on extended Hückel molecular orbital calculations, ER_1 and ER_3 values must be regarded as semiquantitative and were thus not included in the bond enthalpy results in Table VII.

The enthalpies of formation of the nonreorganized ligands, $\Delta H^\circ_f(L^*(g))$, necessary to obtain E(Mo–L), were evaluated through eq 16. The reorganization energies,

$$\Delta H^\circ_f(\text{L}^*(\text{g})) = \Delta H^\circ_f(\text{L}(\text{g})) - \text{ER}_\text{L} \quad (16)$$

ER_L, were estimated by computing the energies of the free and complexed ligands through MNDO calculations.[29] This was not possible for L = C_2H_4 due to the lack of structural data for the complex $Mo(Cp)_2(C_2H_4)$. A different approach for calculating the enthalpy of formation of L* in the case of the alkyl ligands was discussed elsewhere[4] and relies on the use of Laidler terms,[30] E(L–H), in eq 17. As noted before,[4] E(M–L) values based on the

$$\Delta H^\circ_f(\text{L}^*(\text{g})) = E(\text{L–H}) + \Delta H^\circ_f(\text{LH}(\text{g})) - \Delta H^\circ_f(\text{H}(\text{g})) \quad (17)$$

Laidler scheme (see footnote *b* in Table VII) cannot be regarded as physically meaningful quantities. This procedure has, however, the advantage of providing a set of internally consistent E(M–L) data, which can be used to predict enthalpies of formation of organometallic molecules and also to estimate partial bond dissociation enthalpies.[4]

The above-mentioned discrepancies in the enthalpies of formation of the alkyl complexes are reduced by half when the molybdenum–carbon bond enthalpy terms and bond dissociation enthalpies are calculated. In the case of $Mo(Cp)_2Me_2$ the two pairs of independent results for E(Mo–Me) (225 ± 8 and 236 ± 8 kJ mol^{-1}) and $\bar{D}$(Mo–Me) (166 ± 8 and 177 ± 8 kJ mol^{-1}) are in fair agreement. We therefore use their averages E(Mo–Me) = 231 ± 11 kJ mol^{-1} and $\bar{D}$(Mo–Me) = 172 ± 11 kJ mol^{-1} in the following discussion.

It is observed in Table VII that E(Mo–alkyl) values fall in a narrow range, particularly if the uncertainties are considered. In contrast, the molybdenum–carbon bond enthalpy term in $Mo(Cp)_2(C_2Ph_2)$ is about 70 kJ mol^{-1} lower. Interestingly, the Mo–C bond lengths in bis(cyclopentadienyl) complexes with σ-alkyl ligands, ca. 227 pm (see above), are all considerably higher than in $Mo(Cp)_2(C_2Ph_2)$ (214 pm).[31] As noted before for Mo–N and Ti–N bonds,[32] this result stresses the fact that stronger bonds do not necessarily imply shorter bonds when different types of bonding are being compared.

The difference $\bar{D}$(Mo–Me) – $\bar{D}$(Mo–Et) = 16 kJ mol^{-1} (Table VII) can be compared to D(Mo–Me) – (D(Mo–Et) = 18 kJ mol^{-1} in $Mo(Cp)(CO)_3R$,[6d,f,26] $\bar{D}$(Th–Me) – $\bar{D}$(Th–Et) = 21 kJ mol^{-1} in $Th(Cp^*)_2R_2$ ($Cp^* = C_5Me_5$),[6a,26] D(Th–Me) – D(Th–Et) = 19 kJ mol^{-1} in $Th(Cp^*)_2(OBu\text{-}t)R$,[6a,26] and D(Ir–Me) – D(Ir–Et) = 10 kJ mol^{-1} in $Ir(PMe_3)_2(CO)(Cl)(I)R$.[6g,h,26] These differences are close to D(H–Me) – D(H–Et) = 18 kJ mol^{-1} and are in the range of the average D(M–Me) – D(M–Et) value for main-group elements, ca. 20 kJ mol^{-1},[33] suggesting that $\bar{D}$(M–Me) – $\bar{D}$(M–Et) is approximately constant along the periodic table, in the absence of relevant steric effects. The constancy of metal–alkyl bond enthalpy differences (within ca. 10 kJ mol^{-1}) is also indicated by $\bar{D}$(M–Me) – $\bar{D}$(M–Bu) data, available for a few families: 18 kJ mol^{-1} (Table VII), 32 kJ mol^{-1} for $Th(Cp^*)_2R_2$,[6a,26] 33 kJ mol^{-1} for Th-

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(28) (a) Martinho Simões, J. A. *Quim. Nova* **1986**, *9*, 152. (b) Calhorda, M. J. Unpublished calculations.

(29) (a) Calculations for methyl, ethyl, and butyl: Amaral, A.; Soeiro Cordeiro, M. N.; Ramos, M. J. Unpublished results. (b) Calculations for diphenylacetylene: Calhorda, M. J.; Galvão, A. M. Unpublished results.

(30) For methane E(C–H) = 415.83 kJ mol^{-1}, calculated for its enthalpy of atomization. For carbon–hydrogen primary bonds E(C–H) was taken as 410.8 kJ mol^{-1} (Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, New York, 1970).

(31) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850.

(32) Dias, A. R.; Dias, P. B.; Diogo, H. P.; Minas da Piedade, M. E.; Martinho Simões, J. A. *Organometallics* **1987**, *6*, 1427.

(33) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 2.

$(Cp^*)_2(OBu\text{-}t)R$[6a,26] and $U(Me_3SiC_5H_4)_3R$,[6b,26] and 32 kJ mol^{-1} in the case of $Hf(Cp^*)_2R_2$.[6c,26] These values can be compared with *D*(H–Me) – *D*(H–Bu) = 21 kJ mol^{-1}.

In contrast with the approximate constancy of metal–alkyl bond enthalpy differences, there is now experimental[4,6a,c–6h,34–36] and theoretical[37,38] evidence that *D*(M–H) – *D*(M–alkyl) in neutral complexes is significantly dependent on the metal, increasing from early to late transition metals. This trend has been attributed to the fact that a repulsive metal–methyl orbital interaction is reduced in the methyl complexes of early transition metals, due to the high polarity of the metal–methyl bond, leading to an increase of *D*(M–Me) values, relative to *D*(M–H).[37]

As referred to above, the bond enthalpy data in Table VII are anchored in *E*(Mo–Cl) for $MoCl_6$. The choice of this anchor is somewhat arbitrary, implying that the bond enthalpies may be affected by a constant error. Fortunately, absolute bond enthalpy data are often unnecessary to analyze the energetics of many important elementary reaction steps. For example, the enthalpies of β-hydride elimination and olefin insertion (eqs 18 and 19) depend

$$Mo\text{–}C_2H_5 \rightarrow Mo\text{–}H + C_2H_4 \qquad (18)$$

$$Mo\text{–}C_2H_5 + C_2H_4 \rightarrow Mo\text{–}C_4H_9 \qquad (19)$$

on *D*(Mo–Et) – *D*(Mo–H) and *D*(Mo–Bu) – *D*(Mo–Et), respectively. Therefore, any error associated with the estimate of *E*(Mo–Cl) is canceled when the above differences are computed. From $D(C_2H_4\text{–}H) = 151 \pm 4$ kJ mol^{-1} [26] and the results in Table VII, reaction 18 can be predicted to be endothermic by 50 ± 13 kJ mol^{-1}. The entropy term for this reaction is predicted to be $T\Delta S$ = 36 kJ mol^{-1},[39] leading to $\Delta G(18)$ = 14 kJ mol^{-1}. Although the uncertainties in $\Delta H(18)$ and in the entropy estimate do not overrule a negative Gibbs energy change, the result obtained is in keeping with the remarks made on the thermodynamic stability of β-hydrogen-containing dialkyls of the $Mo(Cp)_2$ moiety (see Syntheses). Reaction 19, on the other hand, is predicted to be exothermic by 95 ± 17 kJ mol^{-1} (from the results in Table VII and with $D(C_2H_4\text{–}Et) = 97 \pm 9$ kJ mol^{-1}). The estimated entropy factor in this case is about –41 kJ mol^{-1},[39] indicating that $\Delta G(19)$ = –54 kJ mol^{-1}.

The fact that the difference *D*(M–alkyl) – *D*(M–H) depends on the metal M, being higher for early transition metals, implies that β-hydride elimination is thermodynamically less favorable for these elements and actinides than for late transition metals. For example, $\Delta H(18)$ is about 79 kJ mol^{-1} for $Th(Cp^*)_2R_2$,[6a,26] 87 kJ mol^{-1} for $Zr(Cp^*)_2R_2$,[6c,26,40] 50 kJ mol^{-1} for $Mo(Cp)_2R_2$, 54 kJ mol^{-1} for $Mo(Cp)(CO)_3R$,[6d–f,26] 38 kJ mol^{-1} for $Ir(Cl)(CO)(PMe_3)_2(I)R$,[6g,h,26] and 50 kJ mol^{-1} for *trans*-$Pt(PEt_3)_2(Cl)Et$.[26,41] The approximate constancy of *D*(M–Me) – *D*(M–alkyl), on the other hand, indicates that olefin insertion in a metal–alkyl bond (reaction 19) is less sensitive to the nature of the metal.

Molybdenum–ethylene and molybdenum–acetylene bond dissociation enthalpies shown in Table VII are affected by relatively large errors due to the uncertainties assigned to the estimates of the sublimation enthalpies for the complexes (Table VI). Nevertheless, it is clear that both values are low, in particular the one for ethylene. Perhaps a better comparison between $D(Mo\text{–}C_2H_4)$ and $D(Mo\text{–}C_2Ph_2)$ is the enthalpy of reaction 20, ΔH_r = 56.6

$$Mo(Cp)_2(C_2Ph_2)(c) + C_2H_4(g/soln) \rightarrow Mo(Cp)_2(C_2H_4)(c) + C_2Ph_2(soln) \qquad (20)$$

± 2.5 kJ mol^{-1}, calculated directly from the experimental data. This value should reflect $D(Mo\text{–}C_2Ph_2) - D(Mo\text{–}C_2H_4)$ in solution, under the reasonable assumption that the solution enthalpies of the complexes are similar.

Literature values of *D*(M–alkene) and *D*(M–alkyne) for early and middle transition metals are very scarce. $D(Th\text{–}C_4H_6)$ in the complex $Th(Cp^*)_2(C_4H_6)$ is about 418 kJ mol^{-1}, or 209 kJ mol^{-1} *per double bond*.[7,26] The thorium–methyl *mean* bond dissociation enthalpy in $Th(Cp^*)_2Me_2$, 339 kJ mol^{-1}, is about 130 kJ mol^{-1} higher.[6a,26] This difference is in the range of $\bar{D}(Mo\text{–}Me) - D(Mo\text{–}C_2H_4)$ = 113 kJ mol^{-1}. For late transition elements, the value $D(Pt\text{–}C_2Ph_2) - D(Pt\text{–}C_2H_4)$ = 29 kJ mol^{-1} has been reported for the complexes $Pt(PPh_3)_2L$.[26,42] While this is not far from the difference observed in Table VII, 61 kJ mol^{-1}, particularly if the uncertainities are considered, comparisons relying on estimates of the enthalpies of sublimation of the complexes should be made with caution. The enthalpy of reaction 20 for the platinum compounds is only 11 kJ mol^{-1} endothermic,[42] suggesting that *D*(M–alkyne) – *D*(M–alkene) may indeed be lower for late than for early transition metals.

Molecular Orbital Calculations. The fact that the existence of agostic interactions has been suggested[10] in compounds $W(Cp)_2R_2$ (R = Me, Et), in order to explain their electrochemical behavior, prompted us to look more carefully at the bonding in these and related complexes and at the possibility of such interactions occurring. There is no evidence of agostic bonds in the known structure of the 16-electron $Zr(Cp)_2Me_2$,[43] in the IR and NMR spectra available for $Ti(Cp)_2Me_2$ and $Mo(Cp)_2Me_2^+$,[44,45a] or in the NMR spectra of $Nb(Cp)_2Me_2^+$ and $Mo(Cp)_2Me_2^{2+}$.[45b] Agostic interactions are, however, observed in the rather interesting binuclear complexes containing a bis(cyclopentadienyl)metal fragment bridged to the second metal by a distorted methyl or vinyl group.[46a–c] In the three

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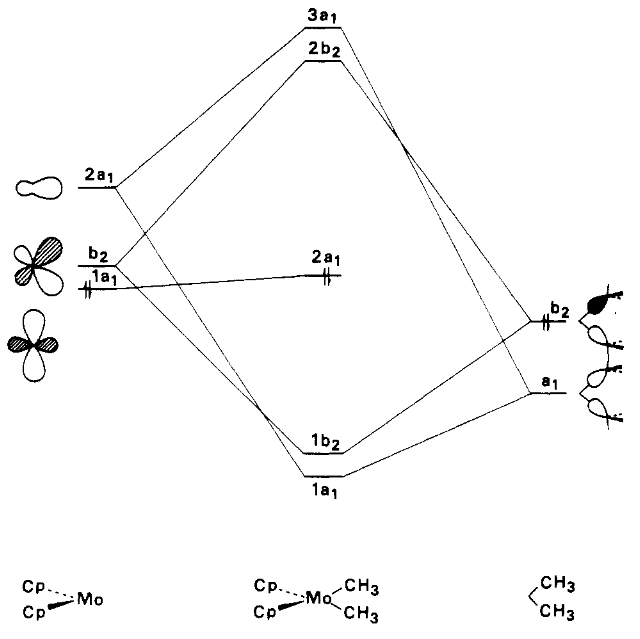


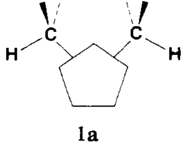
Figure 4. Interaction diagram between a Mo(Cp)$_2$ fragment and two methyl groups.

complexes of this kind, Zr(Cp)$_2$Cl(μ-CH=CMe)ZrCl(C$_5$H$_4$Me)$_2$,[46a] Ti(Cp)$_2$(μ-CH$_2$)(μ-Me)Rh(COD),[46b] and Ti(Cp)$_2$(μ-CH$_2$)(μ-Me)PtMe(PMe$_2$Ph),[46c] one of the protons attached to the bridging carbon is at a close distance from the metal in M(Cp)$_2$, resulting in what is described as an agostic interaction. Recently, a short metal–hydrogen bond was found in the cationic complex Zr(MeC$_5$H$_4$)$_2$[(*Z*)-C(Me)=C(Me)(Pr)](THF)$^+$.[46d] While the zirconium–hydrogen distance, 240 pm, can be considered in the range of agostic interactions (long end), no characteristic spectroscopic features were observed.

β-agostic interactions in mononuclear complexes were recently found in 16-electron species, such as Zr(C$_5$H$_4$Me)$_2$(CH$_2$CH$_2$R)(PMe$_3$)$^+$ and Zr(Cp)$_2$Cl[(SiMe$_3$)C=CPhH].[46e-g]

The calculations done are of the extended Hückel type.[47] Further details are given in the Appendix.

The interaction diagram for the model complex Mo(Cp)$_2$Me$_2$ is shown in Figure 4. The frontier orbitals of the Mo(Cp)$_2$ fragment are well-known,[17] and each methyl group interacts mainly through its lone pair, which gives rise to the symmetric and antisymmetric combinations, a$_1$ and b$_2$, respectively. The bonding results from donation of electrons from these filled fragment orbitals to the empty 2a$_1$ and b$_2$ of Mo(Cp)$_2$, 1a$_1$ becoming slightly antibonding. We shall come back to this point later. The methyl groups were considered as being oriented as shown in **1a**, instead of **1b**, as that geometry leads to a lower energy. This is due to less steric repulsion between the methyl hydrogens and the hydrogen atoms in the Cp rings. We may compare this geometry with the one adopted by the butyl ligands in Mo(Cp)$_2$Bu$_2$ (Figure 2) and see that it is the same: the carbon atoms C(12) and C(22) in the *yz* plane lie closer to the Cp rings.



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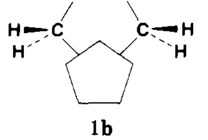

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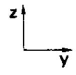


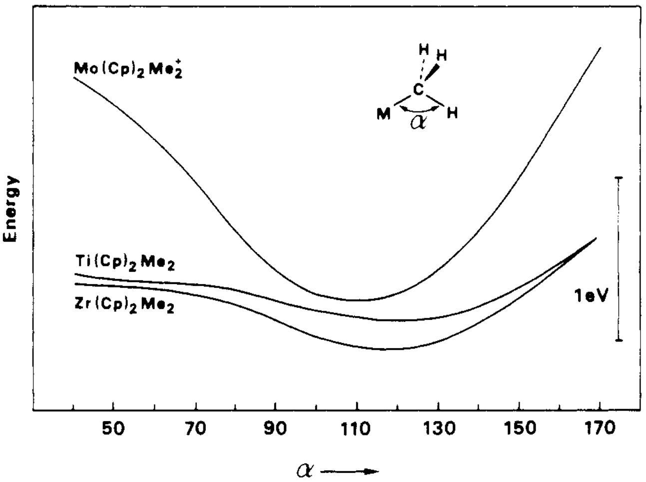
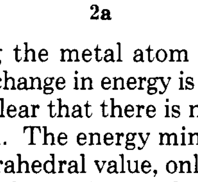
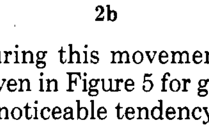


Figure 5. Change in total energy for M(Cp)$_2$Me$_2$ complexes as a function of the M–C–H angle (α).

We can now probe the possibility of forming agostic bonds in similar complexes that have fewer electrons, such as Ti(Cp)$_2$Me$_2$, Zr(Cp)$_2$Me$_2$, or even Mo(Cp)$_2$Me$_2$$^+$. To model this, we allow the methyl group to tilt, changing the M–C–H angle (α, as shown in **2a,b**), the hydrogen approaching the metal atom during this movement. The resulting change in energy is given in Figure 5 for geometry **2a**. It is clear that there is no noticeable tendency toward distortion. The energy minimum occurs for α very close to the tetrahedral value, only slightly larger, as that helps to relieve the steric crowding around the metal. The potential energy curve is quite soft for the 16-electron complex Ti(Cp)$_2$Me$_2$, and that may be an explanation for its great reactivity. A more detailed optimization of the geometry (allowing, for instance, the C–Ti–C angle in *yz* to vary) results in a softer curve but not in a different minimum. For the 17-electron molybdenum or tungsten derivatives there is no indication of an agostic interaction being favored.[10]



2a



2b

We mentioned above the existence of agostic hydrogens in bis(cyclopentadienyl) derivatives, but almost all of them belong to bridging groups in binuclear complexes. Let us consider first the zirconium complex, consisting essentially of two Zr(Cp)$_2$ fragments (in one of them there is a methyl group in the rings) bridged by a substituted vinyl group (**3**; the agostic hydrogen is starred). The important geometrical parameters are the angles shown in **3**, namely Zr–C–C (90.4°, α) Cl–Zr–C (117°, β), and C–C–H (116°, γ). In a typical Zr(Cp)$_2$ derivative, β comes close to 96°. We can then imagine a "nonagostic" geometry for the binuclear complex, where α = 120°, β = 95.6°, and γ = 120°. The relative energies and relevant overlap popula-

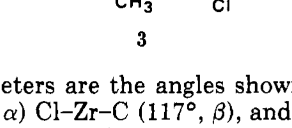


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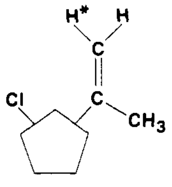
Table VIII. Relative Energies and Overlap Populations of Zirconium Complexes for Agostic and Nonagostic Geometries

	Zr(Cp)$_2$ClL		
	L = Me (5)	L = CMe=CH$_2$ (4)	[Zr(Cp)$_2$Cl]$_2$-(CH=CMe) (3)
	Energy/eV		
agostic	-1212.47	-1390.45	-2673.55
nonagostic	-1212.79	-1390.70	-2672.46
	Overlap Population		
agostic			
Zr-H	0.044	0.067	0.082
Zr-C	0.549		
C-H	0.717	0.725	0.708
nonagostic			
Zr-H	-0.021	-0.026	-0.024
Zr-C	0.576		
C-H	0.768	0.798	0.800

tions for this complex and also for two mononuclear models, Zr(Cp)$_2$Cl(CMe=CH$_2$) (4) and Zr(Cp)$_2$ClMe (5), are shown in Table VIII, for both the agostic and the nonagostic geometries. The result for the monomeric species reminds us of the dimethyl derivatives studied earlier: the undistorted geometry is preferred. The same holds for Ti(Cp)$_2$ClMe, which we also studied, although the curves depicting its behavior are not shown. A common feature of agostic M-Me bonds is the strengthening of the M-C bond involved, the formation of a new M-H bond, and the weakening of the C-H bond, as shown in earlier studies.[48] This does not happen for Zr(Cp)$_2$ClMe. The other two species are different, in that the agostic hydrogens are β, not α. We see that the distortion is favored in the binuclear complex by over 1 eV but is not favored for the mononuclear one. Formation of a weak Zr-H bond is not enough to overcome the energy needed to distort the ligand. This suggests that the observed agostic geometry in the binuclear complex is not driven by electronic factors. On the other hand, replacing the hydrogen in 4 by the Zr(C$_5$H$_4$Me)$_2$Cl fragment to form the binuclear complex induces a few close contacts between atoms (H-Cl = 204, 280 pm and H-H = 206 pm), which are relieved by the distortion (becoming H-Cl = 294, 351 pm and H-H = 278 pm, respectively). Hyla-Kryspin et al. also note the important role played by steric effects in these complexes.[46f]



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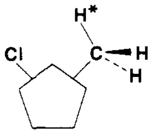

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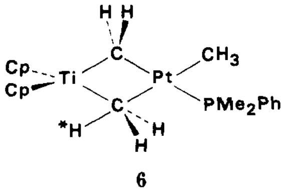
Another complex containing an agostic methyl group is Ti(Cp)$_2$(μ-CH$_2$)(μ-Me)PtMe(PMe$_2$Ph) (6). The possibility of bridging agostic methyls has been theoretically studied[48d] for complexes with a metal–metal bond, similar to the titanium–platinum binuclear derivative, where the two metal atoms are also bonded through CH$_2$ and CH$_3$ bridges.[46c] We considered different geometries for the bridging methyl group having a pentacoordinated carbon and found the experimental geometry to be among the more stable ones. It is not very easy to imagine geometries where the hydrogen is not close to the titanium atom, and our calculations tend to lead us to a titanium–hydride bond.



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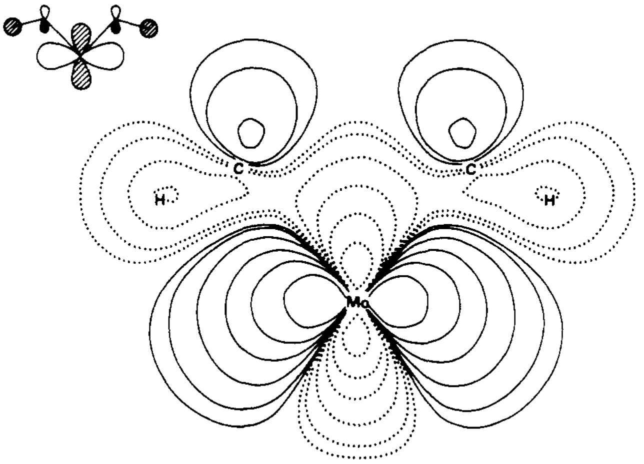
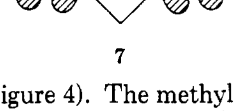


Figure 6. Wave function contour of the Mo(Cp)$_2$Me$_2$ HOMO in the *yz* plane (values for ψ are 0.2, 0.1, 0.055, 0.025, 0.010, and 0.005; the positive and negative signs are indicated by solid and dotted lines, respectively).

The previous results seem to indicate that α-agostic interactions are not favored in terminal alkyls for the M(Cp)$_2$ systems tested and, where agostic hydrogens in bridging groups are found, the distortion appears to be caused mainly by steric effects. This takes us back to the problem of explaining our experimental results. Data from cyclic voltammetry (Table I) show Mo(Cp)$_2$Me$_2$ to be more easily oxidized than the diethyl and the dibutyl derivatives, the difference between these two being very small. Also, if only these are considered, the ease of oxidation follows the inductive effect of the alkyl groups. The dimethyl complex, however, is much more easily oxidized than would have been expected on such grounds. The HOMO of this complex (see molecular orbital diagram in Figure 4) is destabilized relative to 1a$_1$, as it has an antibonding character. This is mainly caused by mixing in an antibonding way of a low-energy symmetric combination of methyl π orbitals (7), which is not shown in the molecular orbital diagram (Figure 4). The methyl group is acting as a π donor, as can be seen in the wave function contour of the HOMO, shown in Figure 6. This also occurs with the dihalide derivatives Mo(Cp)$_2$X$_2$ (X = Cl, Br, I), where the best π donor ligand, Cl, corresponds to the complex with lowest oxidation potential.[13] We do not expect the same to hold for the other alkyl derivatives, due to the different nodal characteristics of the carbon orbitals, and therefore the inductive effects account for the observed easier oxidation of Mo(Cp)$_2$Me$_2$ over Mo(Cp)$_2$Et$_2$. For the mixed Mo(Cp)$_2$XMe derivatives, the π donor capability of the halide is again reflected in the easiest oxidation of the



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chloride compared to the bromide.

Experimental Section

Materials. Mo(Cp)$_2$X$_2$ (X = Cl, Br, I) and Mo(Cp)$_2$(C$_2$Ph$_2$) were prepared from the parent dihydride.[2a,49] Mo(Cp)$_2$Me$_2$ and Mo(Cp)$_2$(C$_2$H$_4$) were obtained from Mo(Cp)$_2$Cl$_2$.[8] The samples for thermochemical measurements were purified according to the following procedures: the dimethyl complex was resublimed at 50 °C under high vacuum; the ethylene and diphenylacetylene complexes were recrystallized several times from pentane and toluene–pentane, respectively. The purity was tested by elemental analysis or ^{1}H NMR spectroscopy. Ethyllithium was prepared from EtBr (Merck) and Li chips (BDH).[50] Butyllithium in hexane (Merck) was stored under Ar and standardized by the method of Gilman.[51]

General Procedures. All manipulations were carried out under Ar with use of standard Schlenk techniques. Column chromatographic separations were done under Ar with silica gel 60/230 ASTM (Merck). Toluene, pentane, diethyl ether, and THF were distilled from Na–benzophenone ketyl. Dichloromethane was distilled from CaH$_2$. Acetonitrile was dried over CaH$_2$ and distilled after refluxing several hours over CaH$_2$–P$_2$O$_5$. Acetone was distilled and kept over 4-Å molecular sieves.

Analytical Procedures. C,H,N analyses were performed in our laboratories. ^{1}H NMR spectra were obtained with a JEOL JN-PS-100 spectrometer (100 MHz). Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using KBr pellets. Mass spectra were measured by the group of Prof. A. Ferrer Correia at the University of Aveiro, Aveiro, Portugal, with a Varian Mat 112S mass spectrometer. ESR spectra were recorded by Dr. M. C. Shohoji with a Bruker ER 200D spectrometer. Gas chromatographic analysis was performed on a Perkin-Elmer Sigma 3B apparatus with a Shimadzu C-R1B recorder/integrator.

Preparation of Mo(Cp)$_2$Bu$_2$. Mo(Cp)$_2$I$_2$ (1.00 g; 2.08 mmol) was suspended in 75 mL of Et$_2$O at −10 °C. LiBu in hexane (4 mL; 1.6 M; 6.40 mmol) was added to the suspension, and the mixture was warmed to room temperature with rapid stirring. After ca. 1 h all the starting diiodide reacted and the solution was orange. The reaction vessel was cooled to −30 °C, and the excess LiBu was destroyed by careful addition of ethanol. The resulting suspension was taken to dryness and the residue extracted with pentane. The orange extract was chromatographed on a silica gel column with pentane as the eluent. The orange band collected was concentrated and cooled to −80 °C to give orange plates. These were filtered off and dried under vacuum. The yields are somewhat unpredictable, typical values being around 300 mg of dibutyl complex (30% based on Mo); mp 88 °C (dec pt 123 °C). Anal. Calcd for C$_{18}$H$_{28}$Mo: C, 63.5; H, 8.3. Found: C, 63.2; H, 8.5. Mass spectrum: *m/z* 342 (^{98}Mo). ^{1}H NMR (C$_6$D$_6$): δ 1.59–0.34 (m, 18 H, Bu), 4.07 (s, 10 H, Cp).

Preparation of Mo(Cp)$_2$Et$_2$. The procedure was exactly as described for the dibutyl complex but with LiEt (0.5 M in pentane) instead of LiBu. The yield is around 15%, based on Mo; mp 123 °C dec. Anal. Calcd for C$_{14}$H$_{20}$Mo: C, 59.2; H, 7.1. Found: C, 59.4, H, 7.2. Mass spectrum: *m/z* 286 (^{98}Mo). ^{1}H NMR (C$_6$D$_6$): δ 0.69 (q, J_{HH} = 7 Hz, 4 H, CH$_2$), 1.37 (t, J_{HH} = 7 Hz, 6 H, Me), 4.5 (s, 10 H, Cp).

Preparation of Mo(Cp)$_2$ClMe. Dropwise addition of a solution of HCl in Et$_2$O (1.2 M; 490 μL; 0.59 mmol) to a solution of Mo(Cp)$_2$Me$_2$ in the same solvent (0.166 g; 0.65 mmol) gave pink-brown crystals. The solution was filtered off, and the crystals were dried under vacuum. The yield is quantitative. Anal. Calcd for C$_{11}$H$_{13}$ClMo: C, 47.7; H, 4.7. Found: C, 47.2; H, 4.8. ^{1}H NMR ((CD$_3$)$_2$CO): δ 0.14 (s, 3 H, Me), 5.00 (s, 10 H, Cp).

Preparation of Mo(Cp)$_2$(O$_2$CPh)Me. A solution of Mo(Cp)$_2$Me$_2$ (0.168 g; 0.65 mmol) and benzoic acid (0.080 g; 0.65 mmol) in 25 mL of toluene was warmed to 70 °C for 15 h. After evaporation to dryness the residue was extracted with Et$_2$O and the solution concentrated and cooled to −50 °C to give red-brown crystals. These were filtered off and dissolved in dichloromethane, and the solution was chromatographed on a SiO$_2$ column with ethanol as eluent. The eluate was taken to dryness under vacuum; yield 60%. ^{1}H NMR (CDCl$_3$): δ 0.32 (s, 3 H, Me), 5.07 (s, 10 H, Cp), 7.87–7.96 (m, 5 H, Ph).

Preparation of Mo(Cp)$_2$BrMe. EtMgBr in Et$_2$O (1.0 mL; 0.70 mmol) was added to a solution of Mo(Cp)$_2$(O$_2$CPh)Me (0.200 g; 0.55 mmol) in 20 mL of Et$_2$O. After 1 h the white precipitate formed was filtered off and the resulting solution cooled to −50 °C to give green crystals. These were filtered, washed with pentane, and dried under vacuum; yield 80%. Anal. Calcd for C$_{11}$H$_{13}$BrMo: C, 41.2; H, 4.1. Found: C, 40.7; H, 4.00. ^{1}H NMR (CD$_3$CN): δ 0.18 (s, 3 H, Me), 4.98 (s, 10 H, Cp).

Preparation of Mo(Cp)$_2$BuMe. A solution of Mo(Cp)$_2$ClMe (0.409 g; 1.48 mmol) in Et$_2$O (30 mL) at −30 °C was treated with LiBu in hexane (1.6 M; 1.3 mL; 2.08 mmol) and the mixture warmed to room temperature. After ca. 1 h, the solution was cooled to −50 °C and excess LiBu destroyed by careful addition of ethanol. The mixture was brought back to room temperature and evaporated to dryness. The residue was extracted with pentane and the solution concentrated and cooled to −80 °C to give an orange solid, which was sublimed twice at ca. 60 °C (0.1 Pa): yield 30%; mp 82 °C. Anal. Calcd for C$_{15}$H$_{22}$Mo: C, 60.4; H, 7.4. Found: C, 60.4; H, 7.4. Mass spectrum: *m/z* 300 (^{98}Mo). ^{1}H NMR (C$_6$D$_6$): δ 0.01 (br, 3 H, Mo–Me), 0.8 (br, 2 H, Mo–CH$_2$), 1.09 (t, 3 H, CH$_2$C*H*$_3$), 1.34, 1.46 (m, 4 H, C*H*$_2$C*H*$_2$), 4.08 (s, 10 H, Cp).

Preparation of [Mo(Cp)$_2$Bu$_2$][PF$_6$]. A solution of [Fe(Cp)$_2$][PF$_6$] (0.033 g; 0.10 mmol) in acetone was added to a solution of Mo(Cp)$_2$Bu$_2$ (0.041 g; 0.12 mmol) in the same solvent (5 mL), with stirring. The resulting orange mixture was evaporated to dryness and washed with toluene (3 × 5 mL) and diethyl ether (3 × 5 mL) to extract ferrocene and excess Mo(Cp)$_2$Bu$_2$. The orange residue was recrystallized from acetone–ethanol. The yield was quantitative with respect to added [Fe(Cp)$_2$][PF$_6$]. Anal. Calcd for C$_{18}$H$_{28}$MoF$_6$P: C, 44.5; H, 5.8. Found: C, 44.9; H, 5.8. ESR: $g_\parallel$ = 2.07 (9); $g_\perp$ = 2.00 (7).

Preparation of [Mo(Cp)$_2$Et$_2$][PF$_6$] and [Mo(Cp)$_2$ClMe][PF$_6$]. These complexes were prepared as described for the dibutyl analogue, always in quantitative yields. Anal. Calcd for C$_{14}$H$_{20}$MoF$_6$P: C, 39.1; H, 4.7. Found: C, 38.8; H, 4.5. ESR: $g_\parallel$ 2.01 (1); $g_\perp$ = 2.04 (1). Anal. Calcd for C$_{11}$H$_{13}$MoClF$_6$P: C, 31.3; H, 3.1. Found: C, 31.1; H, 3.2. ESR: g = 1.9634.

Electrochemistry. The electrochemical instrumentation consisted of a PAR 173 potentiometer, a PAR 175 voltage programmer, a PAR 179 digital coulometer, and a Houston Instruments Omnigraphic 2000 X-Y recorder. Potentials were referred to a calomel electrode (SCE) containing a saturated solution of potassium chloride. The experimental setup was checked against a 1.0 × 10^{-3} M solution of ferrocene and LiClO$_4$ (0.10 M) in acetonitrile. The ferrocenium/ferrocene potential was in agreement with the literature.[52]

The electrochemical experiments on each complex were followed by addition of ferrocene to the solution, and a new cyclic voltammogram was recorded. The electrochemical behavior of the complexes did not seem to be affected by the presence of ferrocene and vice versa. The characteristic wave ferrocenium/ferrocene was observed at $E_{p/2}$ = 435 mV vs SCE and i_a/i_c = 1.00 at 100 mV s^{-1}, under the experimental conditions.

The working electrodes were a 2-mm piece of Pt wire and Pt gauze for the cyclic voltammetry and the coulometry experiments, respectively. The auxiliary electrode was a Pt wire coil. Cyclic voltammetry experiments were performed in a PAR polarographic cell, at room temperature. The solutions used were 1 mM in solute and 0.1 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate. Coulometry experiments were done in a three-compartment cell, where the working electrode compartment was separated from the compartment for auxiliary and reference electrodes by medium-porosity glass frits. Solvents were dried as described above. Solutions were degassed with dry nitrogen before each experiment, and a N$_2$ atmosphere was maintained over the solution during the experiments.

Crystallography. Single crystals of Mo(Cp)$_2$Bu$_2$, [C$_{18}$H$_{28}$Mo], M_r = 340.36, were grown from a saturated solution in ethanol at

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−20 °C, under an argon atmosphere. The crystals are monoclinic, space group $C2/m$, with a = 2160.8 (7) pm, b = 786.3 (3) pm, c = 1955.2 (8) pm, β = 100.65 (3)°, $V = 3264.7 \times 10^6$ pm^3, Z = 8, D_c = 1.39 g cm^{-3}, and μ(Mo Kα) = 7.03 cm^{-1}.

All X-ray measurements were made with an Enraf-Nonius CAD-4 diffractometer and graphite-monochromatized Mo Kα radiation (λ = 71.069 pm). Cell dimensions and orientation matrices were obtained by least-squares refinement of setting angles for 25 automatically centered reflections with $9 < \theta < 13°$. The intensities of 3451 independent reflections in the range $1.5 < \theta < 28°$ ($+h,+k,\pm l$) were measured by the ω–2θ scan mode. The data were corrected for Lorentz and polarization effects and empirically for absorption.

A total of 3253 reflections satisfied the criterion $F > 3\sigma(F)$ and were used for the structure solution and refinement. The Mo position was located from a Patterson map, and the C positions were found from subsequent difference Fourier syntheses. Least-squares refinements with isotropic temperature factors for all the non-hydrogen atoms gave R = 0.075. Refinement was continued with anisotropic thermal parameters to give R = 0.045. H atoms were inserted in idealized positions, the positional coordinates being refined with fixed isotropic temperature factors and a fixed distance to the parent carbon atom. The weighting scheme $w = 4.502/(\sigma^2|F| + 0.000\,129)$ was found to give acceptable agreement analysis. The reflections 111, 400, $\bar{1}13$, $\bar{2}02$, 202, and 004, thought to be suffering from extinction, were removed from the data. Final refinement gave R = 0.025 and R_w = 0.034 ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$). The largest shift/error on a non-hydrogen atom (Z/C, C(14)) in the final cycle was 0.11, and the largest peak in the final difference Fourier synthesis was 0.53×10^{-6} e pm^{-3}. Tables of anisotropic displacement factor coefficients and positional parameters for the hydrogen atoms and lists of observed and calculated structure factors are supplied as supplementary material. All computations required to solve and refine the structure were made with SHELX76;[53] drawings were made with use of ORTEPII.[54] Atomic scattering values were taken from ref. 55.

Vapor Pressure Measurements. The Knudsen cell setup is a modified version of the one previously reported.[18,19] The Mo(Cp)$_2$Et$_2$ vapor effused through a circular hole with an area of 4.54×10^{-3} cm^2, drilled in a 2.09×10^{-3} cm thick copper foil soldered on a bronze lid. The temperature was controlled to ±0.01 K by a Haake ED Unitherm thermostat and measured to ±0.01 K with a calibrated mercury thermometer. The mass loss was determined by weighing the cell to $\pm 10^{-5}$ g with a Sartorius 2474 balance. No signs of decomposition of the complex were observed during the runs. Under the same conditions Mo(Cp)$_2$Bu$_2$ does not sublime and instead decomposes at higher temperatures (>60 °C).

Calorimetry. The reaction-solution calorimeter previously described,[27] with a redesigned head,[19] was used to measure the reaction and solution enthalpies. Modifications included a better sealed stirrer and a second inlet, closed by a septum, enabling us to sample the gas phase with an Hamilton syringe for gas chromatography analysis. When iodine–toluene solutions were used as the calorimetric solvent, the inert atmosphere inside the calorimetric vessel was ensured by bubbling argon through the solution for about 45 min before each run. HCl–isopropyl ether solutions were transferred, under an inert atmosphere, from a Schlenk type buret to the argon-flushed calorimetric vessel. The glass bulbs containing the samples were sealed under argon.

The hydrochloric acid solutions were prepared by bubbling dry HCl in isopropyl ether distilled under argon over Na–benzophenone ketyl. The gaseous HCl was produced by reaction of sulfuric acid with anhydrous NaCl and passed through two traps, containing concentrated H$_2$SO$_4$ and dry ice, respectively.

The method used to determine the amount of ethylene in the gas phase and in solution, for the reaction of Mo(Cp)$_2$(C$_2$H$_4$) with I$_2$, was as follows. A 412-mL glass reservoir, closed with a GC septum, was evacuated and filled with ethane (the internal standard), at ambient temperature and pressure. The temperature was measured to ±0.1 °C with a mercury thermometer and the pressure to ±0.05 Torr with a Short & Masson barometer. The amount of ethane inside the reservoir was calculated by the ideal gas law. At the end of an experiment, 10 mL of the gas phase (50 mL total volume) was sampled from the calorimeter and injected in the reservoir. Three samples of this mixture, with volumes in the range of 40–750 μL, were sequentially injected in the gas chromatographic apparatus (column Porapak Q, Waters Associates). The mass (m_{ethane}) related to the area of the ethane peak (A_{ethane}) was calculated from the correlation

$$m_{\text{ethane}}\ (\text{g}) = [(7.38 \pm 0.20) \times 10^{-11}]A_{\text{ethane}} + (0.61 \pm 0.12) \times 10^{-5}$$

obtained by calibrating the GC analyzer with known amounts of pure ethane. The amount of ethylene was derived from

$$m_{\text{ethylene}}\ (\text{g}) = m_{\text{ethane}}(A_{\text{ethylene}}/A_{\text{ethane}})$$

after testing that the detector response factors for ethane and ethylene were similar. The total number of moles of gaseous ethylene inside the calorimeter was then calculated from the volumes of samples injected in the reservoir and in the chromatographic apparatus, and from the gas-phase volume in the calorimetric vessel.

The calorimeter was opened after the gas-phase analysis, and three samples of the liquid (1–10 μL) were injected in the GC analyzer (column SE 30, Altech Associates). The total amount of ethylene dissolved was calculated as described above, with use of the solvent as internal standard (125 mL of toluene in the calorimetric vessel):

$$m_{\text{toluene}}\ (\text{g}) = [(6.69 \pm 0.44) \times 10^{-11}]A_{\text{toluene}} + (1.09 \pm 0.78) \times 10^{-4}$$

This analysis was performed on two of the five calorimetric experiments only. In both cases the stoichiometric amount of ethylene evolved was 8.7×10^{-5} mol. The obtained results (run 1, liquid phase 7.1×10^{-5} mol, gas phase 1.3×10^{-5} mol; run 2, liquid phase 6.2×10^{-5} mol, gas phase 1.9×10^{-5} mol) indicated that the reaction of Mo(Cp)$_2$(C$_2$H$_4$) with I$_2$ was quantitative and that ca. 80% of ethylene remained in the liquid phase.

The molar ratio $n(\text{g})/n(\text{l})$ of methane, ethane, or butane in the gas phase and in solution for the reactions of Mo(Cp)$_2$Me$_2$, Mo(Cp)$_2$Et$_2$, and Mo(Cp)$_2$Bu$_2$ with HCl was determined (two calorimetric experiments in each case) by injecting samples of both phases in a SE 30 column. The calculation was based on

$$n(\text{g})/n(\text{l}) = A(\text{g})\ V(\text{g})\ v(\text{l})/[A(\text{l})\ V(\text{l})\ v(\text{g})]$$

where A is the area of a peak, v the volume injected, and V the total volume of the gas (50 mL) and liquid (125 mL) phases. The results indicate that 55% of methane, 80% of ethane, and 99.5% of butane were dissolved in the HCl–isopropyl ether mixture at the end of the reactions.

Table IX. Exponents and Parameters for Ti, Zr, and Mo

orbital	$-H_{ii}$/eV	ζ_1	ζ_2	C_1	C_2
Ti 4s	8.97	1.075			
Ti 4p	5.44	0.675			
Ti 3d	10.81	4.55	1.40	0.4206	0.7839
Zr 5s	10.10	1.817			
Zr 5p	6.86	1.776			
Zr 4d	12.10	3.835	1.505	0.6214	0.5793
Mo 5s	8.77	1.96			
Mo 5p	5.60	1.90			
Mo 4d	11.06	4.54	1.90	0.5899	0.5899

Acknowledgments. We thank Prof. A. Ferrer Correia for the mass spectra and Prof. M. C. Shohoji for the ESR spectra. Our work has been supported by the Instituto Nacional de Investigação Científica, Portugal. A.M.G. thanks the Junta Nacional de Investigação Científica e Tecnológica for a grant.

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Appendix

All the calculations were of the extended Hückel[47] type with modified H_{ij}'s.[56] The basis set for the metal atoms consisted of ns, np, and $(n - 1)$d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometries of $M(Cp)_2Me_2$ complexes were modeled after those known ($Zr(Cp)_2Me_2$,[43] $Mo(Cp)_2Bu_2$). The distances (pm) and the angles (deg) used were as follows: M–Cp = 207 (Ti), 222 (Zr), 200 (Mo); C–C(Cp) = 140; C–H(Cp) = 108; M–C = 220 (Ti), 228 (Zr), 228 (Mo); C–H(Me) = 109; Cp–M–Cp = 133 (Ti), 132.5 (Zr), 132 (Mo); C–M–C = 80 (Ti), 95.6 (Zr), 80 (Mo). A more complete study was done for the Ti derivative, in which simultaneous variation of the C–Ti–C angle and agostic deformation were tested, without major changes in the result shown for a fixed geometry. The geometries of the binuclear complexes were taken from the experimentally determined ones.

Standard parameters were used for C and H,[47] while those for the metals are listed in Table IX.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atomic coordinates, and bond lengths involving hydrogen (3 pages); a table of structure factors (14 pages). Ordering information is given on any masthead page.

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Steric Factors in Neutral and Anionic Alkyne Complexes of Tungsten(0)[1]

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Received June 22, 1990

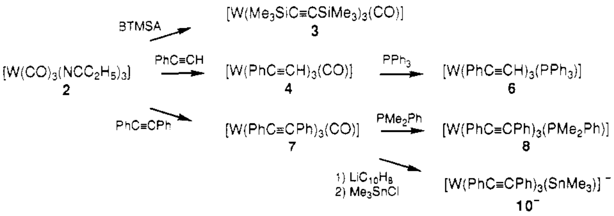
The labile W(0) source $[W(CO)_3(NCC_2H_5)_3]$ (**2**) reacts with the bulky alkyne bis(trimethylsilyl)acetylene (BTMSA) under reduced pressure to give the tris(alkyne) complex $[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$ (**3**), which has a low barrier to alkyne rotation. The terminal alkyne $PhC{\equiv}CH$ reacts similarly with **2** to give the tris(alkyne) complex $[W(PhC{\equiv}CH)_3(CO)]$ (**4**), isolated as an oil and derivatized by substitution with PPh_3 to give $[W(PhC{\equiv}CH)_3(PPh_3)]$ (**6**). Complex **6** is monoisomeric, with all three alkynes oriented with the acetylenic hydrogens proximal to the phosphine, while **4** exists as a mixture of isomers. ^{13}C NMR spectroscopy indicates that **4** exists in $C_6D_5CD_3$ as a mixture of $\mathbf{4}^3$ (4%), $\mathbf{4}^2$ (64%), and $\mathbf{4}^1$ (32%), with three, two, and one acetylenic hydrogen, respectively, proximal to the carbonyl. Phosphine substitution is also feasible with the more sterically crowded tris(alkyne) substrate $[W(PhC{\equiv}CPh)_3(CO)]$ (**7**), which reacts with PMe_2Ph to give $[W(PhC{\equiv}CPh)_3(PMe_2Ph)]$ (**8**), in which $\Delta G^{\ddagger}$ for alkyne rotation is 13.2 (3) kcal mol^{-1}. The importance of steric factors in determining bonding interactions and alkyne rotation barriers in $[W(RC{\equiv}CR)_3(L)]$ complexes was evaluated by comparison of the NMR characteristics of $[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$ ($\mathbf{9}^-$) with those of $[W(PhC{\equiv}CPh)_3(SnMe_3)]^-$ ($\mathbf{10}^-$), prepared by naphthalenide reduction of **7** and addition of Me_3SnCl. The alkyne rotation barrier in $\mathbf{10}^-$ ($\Delta G^{\ddagger}$ = 12.7 (2) kcal mol^{-1}) is similar to that in $\mathbf{9}^-$ ($\Delta G^{\ddagger}$ = 13.1 kcal mol^{-1}), implying that steric factors are not dominant. NMR parameters involving ^{119}Sn suggest that $\mathbf{9}^-$ and $\mathbf{10}^-$ are best thought of as complexes of "$[W(PhC{\equiv}CPh)_3]$" with R_3Sn^- anions.

Introduction

It has been known for many years that the reaction of alkynes with $[W(CO)_3(NCCH_3)_3]$, a labile W(0) source, leads to the formation of tetrahedral tris(alkyne) complexes of the type $[W(RC{\equiv}CR')_3(CO)]$,[2] and the study of these complexes has been important in the development of our understanding of the bonding interactions between alkynes and transition-metal centers, particularly in the ability, unique amongst η^2 ligands, to act as four-electron donors.[2-6]

The original syntheses of tris(alkyne) complexes of W(0) included diphenylacetylene, methylphenylacetylene, and 3-hexyne ligands, and variations have subsequently led to complexes containing hexafluorobutyne ligands[7] and a crown ether alkyne ligand.[8] Reduction of $[WCl_4(PMe_3)_2]$ by sodium amalgam in the presence of $PhC{\equiv}CH$ has also been used to prepare the tris(phenylacetylene) complex $[W(PhC{\equiv}CH)_3(PMe_3)]$[9]—the success of this complementary route confirms that the $[W(RC{\equiv}CR')_3(L)]$ stoichiometry is particularly stable.

Scheme I



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