110317-19-6; 9, 110317-21-0; 10, 110317-22-1; 11, 110317-23-2; 12, 110317-26-5; 13, 110317-24-3; $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$, 87105-61-1; $[Au(C_6F_5)(tht)]$, 60748-77-8; [AuCl(tht)], 39929-21-0; $[Ag(OClO_3)PPh_3]$, 73165-02-3; $[Ph_2PCH_2PPh_2CH_2COOMe]Cl$, 110317-31-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, and bond angles (4 pages); a listing of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

Reactivity of a Labile Molybdenocene Olefin Complex with Organic π-Acceptors

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The reactivity of highly labile molybdenocene (Z)-stilbene complex $Cp_2Mo[\eta^2\text{-}(Z)\text{-}C_6H_5CH{=}CHC_6H_5]$ (1) ($Cp = \eta^5\text{-}C_5H_5$) with organic acceptor molecules has been investigated. 1 reacts readily with various olefinic and heteroolefinic ligands L to give molybdenocene complexes of the formula Cp_2MoL (L = formaldehyde, nonenolizable ketones, benzalanilide, and thiobenzophenone). Spectroscopic data indicate dihapto coordination of L at the Cp_2Mo fragment via C=C, C=N, C=O, and C=S bonds. Protic substances and some strong acceptors induce a Z–E isomerization of coordinated (Z)-stilbene in 1, resulting in the formation of the (E)-stilbene complex $Cp_2Mo[\eta^2\text{-}(E)\text{-}C_6H_5CH{=}CHC_6H_5]$ (2) which is significantly less labile than the (Z)-stilbene complex. Maleic anhydride catalyzes this isomerization reaction rapidly and cleanly. Extremely electrophilic ketones R_2CO ($R = CO_2C_2H_5$, CF_3) are head-to-head coupled at the divalent molybdenum center of 1 to afford molybdenocene diolato complexes $Cp_2Mo(O_2C_2R_4)$ exclusively. The reaction of 1 with 9,10-phenanthrenequinone gives the enediolato complex $Cp_2Mo(O_2C_{14}H_8)$ of which the oxidation electrochemistry was studied.

Introduction

The metallocene of molybdenum Cp_2Mo ($Cp = \eta^5\text{-}C_5H_5$) was electronically and structurally characterized by infrared, ultraviolet–visible, and magnetic circular dichroism spectra using matrix isolation methods.[2] The 16-electron species molybdenocene has previously been postulated as a reactive intermediate in the two-electron reduction of molybdenocene dichloride Cp_2MoCl_2,[3] the reductive elimination of alkane RH from an alkyl hydride $Cp_2MoR(H)$,[4,5] the photolysis of the carbonyl Cp_2MoCO,[6] and the photoelimination of dihydrogen from the dihydride Cp_2MoH_2.[7] In the presence of two-electron ligands L these reactions give low-valent molybdenocene complexes of the type Cp_2MoL, whereas in the absence of any suitable ligand, a so-called dehydromolybdenocene dimer $[CpMo(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ is formed.[8] The reactivity pattern of molybdenocene in solution thus appears to be dominated by an addition reaction of ligand L and by a dimerization reaction which can be viewed as self-insertion of one monomeric molybdenocene unit into the C–H bond of another. With the aid of flash photolysis experiments on the dihydride Cp_2MoH_2, molybdenocene has also been detected as a short-lived species in solution.[9]

Recently, we have described the synthesis and some properties of an unusually labile molybdenocene olefin complex, viz. the (Z)-stilbene adduct of molybdenocene $Cp_2Mo[\eta^2\text{-}(Z)\text{-}C_6H_5CH{=}CHC_6H_5]$ (1). Its high reactivity has been utilized for the preparation of acetylene complexes of molybdenocene $Cp_2Mo(\eta^2\text{-}RC{\equiv}CR')$ in a very general way.[10] The observation that the olefinic ligand in 1 is very easily lost giving the dimerization product of molybdenocene and that various acetylenes $RC{\equiv}CR'$ replace (Z)-stilbene under mild conditions suggested to us to regard the (Z)-stilbene complex 1 as a synthetically useful versatile functional equivalent of monomeric molybdenocene. In order to explore further the reactivity of 1, we investigated its reaction with a selection of organic substrates functioning as good π-acceptors such as olefins and heteroolefins. Since metal–ligand bonding in Cp_2MoL type complexes is mainly stabilized by back bonding from the electron-rich d^4-metal center of the Cp_2Mo fragment to the acceptor orbital of the ligand L,[11] we hoped that with these ligands 1 would easily undergo substitution reactions to give low-valent molybdenocene complexes.

In this paper we wish to report the extension of the ligand replacement reaction leading to a number of new

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(2) (a) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1982**, *21*, 3647. (b) Cox, P. A.; Grebenik, P.; Perutz, R. N.; Robinson, M. D.; Grinter, R.; Stern, D. R. *Inorg. Chem.* **1983**, *22*, 3614.
(3) (a) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (c) Thomas, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5943. (d) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.
(4) (a) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886. (b) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 7262. (c) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975/76**, *1*, 285.
(5) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747.
(6) Wong, K. L. T.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*. 3694.
(7) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.
(8) (a) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Meunier, B.; Prout, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2558.
(9) Perutz, R. N.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 457.
(10) Herberich, G. E.; Okuda, J. *Chem. Ber.* **1984**, *117*, 3112.
(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

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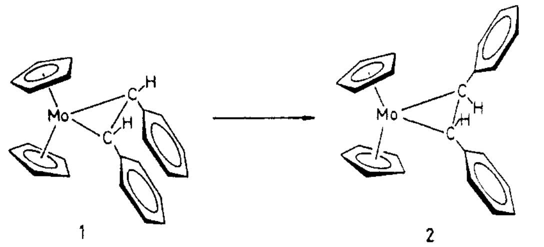
low-valent complexes of the type Cp_2MoL, including a formaldehyde complex, a remarkable *Z–E* isomerization of the coordinated (*Z*)-stilbene, and some oxidation reactions taking place at the divalent molybdenum atom of **1**. Parts of this work have been reported previously.[12]

Results and Discussion

Reaction with Olefins. *Z–E* Isomerization. When dimethyl fumarate is reacted with **1** in toluene at 50 °C a smooth replacement reaction occurs and the dimethyl fumarate complex of molybdenocene, $Cp_2Mo[\eta^2\text{-}(E)\text{-}H_3CCO_2CH{=}CHCO_2CH_3]$, is formed besides free (*Z*)-stilbene. Melting point, ^1H NMR, IR, and mass spectral data of the isolated product agreed in all respects with an authentic sample prepared according to Nakamura and Otsuka by reacting molybdenocene dihydride with the ester.[4] Analogously, **1** undergoes clean substitution reaction with other activated olefins such as methyl acrylate, acrylonitrile, methyl (*E*)-cinnamate, and fumaronitrile, while olefins lacking electron-withdrawing groups like ethylene and styrene reacted only sluggishly with **1**.[13] As was noted for the substitution reaction of **1** with acetylenes,[10] the substitution reaction of activated olefins does not follow a simple dissociative pathway. Addition of a large excess of (*Z*)-stilbene did not influence the rate of the replacement reaction of **1**.

When stoichiometric amounts of maleic anhydride are mixed with a C_6D_6 solution of **1** at room temperature, a very fast and complete conversion of **1** to the isomeric (*E*)-stilbene complex of molybdenocene, $Cp_2Mo[\eta^2\text{-}(E)\text{-}C_6H_5CH{=}CHC_6H_5]$ (**2**), is observed by ^1H NMR within a few minutes (eq 1). Subsequently, we discovered also



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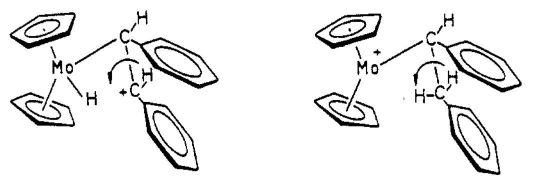
that maleic anhydride is capable of converting **1** to **2** catalytically. In a typical experiment a 0.3 M C_6D_6 solution of **1** is quantitatively isomerized to **2** using 15 mol % maleic anhydride within 15 min. The (*E*)-stilbene complex **2** can be readily isolated after chromatographic workup as brown crystals which are significantly less sensitive to air, heat, and light than the (*Z*)-stilbene complex **1**. The ^1H and ^{13}C NMR spectra of **2** reveal only one signal for both Cp rings confirming their equivalence due to C_2 point symmetry of this molecule. The electron impact mass spectrum shows the ion *m/e* 406 demonstrating also a higher stability of **2** in comparison with **1**, which failed to give any evidence for the molecular ion under the same conditions.[10]

The catalytic isomerization of **1** to **2** is not significantly influenced by solvent variation nor by addition of excess (*E*)-stilbene and other potential ligands for the Cp_2Mo fragment like carbon disulfide[14] and acetylenes.[10] These findings suggest strongly that the (*Z*)-stilbene in **1** remains within the coordination sphere of the Cp_2Mo unit during the actual *Z–E* isomerization step. When the (*Z*)-stilbene complex **1** is heated to 50 °C in the presence of a large excess of (*E*)-stilbene for 24 h, the main reaction is the thermolysis of **1** to give the dehydromolybdenocene dimer besides molybdenocene dihydride and only about a 10% yield of **2** is obtained. Thus, dissociation of (*Z*)-stilbene from **1** followed by external *Z–E* isomerization and complexation of (*E*)-stilbene to free molybdenocene seems to be rather improbable.

In the course of our studies on the reactivity of **1** we have found that this remarkable *Z–E* isomerization is induced by other strong π-acceptor molecules like 1,2-diketones and by all protic substances such as weak acids and even enolizable ketones (vide infra). In none of the cases studied, however, have we been able to find a catalytic conversion of **1** to **2** as efficient and clean as we have observed with maleic anhydride. While with other π-acceptors different reactions may take place as parallel reactions as specified further below, the use of protic reagents is often accompanied by the formation of intractable decomposition products. As a mechanistic explanation for this isomerization reaction we propose a direct interaction of the isomerization reagent with the (*Z*)-stilbene complex **1**. In the case of strong π-acceptors, in particular maleic anhydride, a single-electron transfer from the d^4 metal center of **1** to the acceptor molecule X via preceding charge-transfer interaction is supposed to result in the formation of a radical pair within the solvent cage $\{Cp_2Mo[(Z)\text{-}C_6H_5CH{=}CHC_6H_5]^{+\bullet}X^{-\bullet}\}$. The decreased back bonding from this d^3 molybdenum center to the (*Z*)-stilbene ligand then would facilitate the rotation around the carbon–carbon bond of the olefin. For the acid-induced *Z–E* isomerization reaction we assume formally d^2 intermediates as depicted below. One possible species in which the



rotation barrier of the carbon–carbon bond of the (*Z*)-stilbene is lowered due to one weakened molybdenum–carbon bond results from the protonation of the d^4 metal center in **1**. The other conceivable intermediate is a product of a consequent insertion of the olefin into the Mo–H bond to give an alkyl cation exhibiting a 1,2-diphenylethyl ligand that after the rotation around the carbon–carbon single bond, β-elimination, and deprotonation, could give the (*E*)-stilbene complex **2**. It has been shown that the ethylene complex of molybdenocene $Cp_2Mo(\eta^2\text{-}C_2H_4)$ can be reversibly protonated to the hydrido cation $[Cp_2Mo(H)(\eta^2\text{-}C_2H_4)]^+$.[15a] Moreover, the styrene ligand in the related d^2 niobocene complex $(\eta^5\text{-}C_5Me_5)_2Nb(H)(\eta^2\text{-}C_6H_5C_2H_3)$ does perform a *Z–E* isomerization in the metal–ligand sphere via reversible insertion and β-H elimination.[15b] The driving force for the isomerization can be ascribed to the higher thermodynamic stability of the (*E*)-stilbene complex **2**. This stems from the lesser steric encumbrance in **2** with only one phenyl ring being in close proximity to each of the Cp ligands of the sterically rather compact Cp_2Mo fragment, while the steric constraint imposed by two phenyl rings on only one Cp ring in the (*Z*)-stilbene complex **1** should be extremely high, as evidenced by the unusual lability of **1** reflecting a weakened Cp_2Mo–ligand bonding. In addition, (*E*)-stilbene is considered to be a better π-acceptor than

(12) Herberich, G. E.; Okuda, J. *Angew. Chem.* **1985**, *97*, 400; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402.
(13) $Cp_2Mo(\eta^2\text{-}C_2H_4)$ can be prepared according to ref 3b and ref 15. $Cp_2Mo(\eta^2\text{-}C_6H_5C_2H_3)$ is accessible by the reaction of the dihydride Cp_2MoH_2 and phenylacetylene, cf. ref 10.
(14) Okuda, J.; Herberich, G. E. *J. Organomet. Chem.* **1987**, *320*, C35.
(15) (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

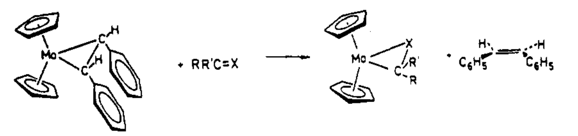
Table I. ^{1}H NMR and IR Spectroscopic Data

compound	^{1}H NMR[a] Cp	^{1}H NMR[a] others	IR (KBr), cm^{-1}
$Cp_2Mo[\eta^2\text{-}(E)\text{-}C_6H_5CHCHC_6H_5]$ (2)	4.03	3.81 (s, 2, CH_2) 6.82–7.28 (m, 10, C_6H_5)[b]	
$Cp_2Mo(\eta^2\text{-}C_6H_5COCF_3)$ (3)	4.48, 4.98[c]	6.91–7.58 (m, 5, C_6H_5)	1140 (ν(CF))
$Cp_2Mo(\eta^2\text{-}C_6H_5COCO_2CH_3)$ (4)	4.54, 4.86	3.59 (s, 3, CH_3) 6.83–7.90 (m, 5, C_6H_5)	1686 (ν(CO))
$Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CO]$ (5)	4.68	6.94–8.18 (m, 10, C_6H_5)	
$Cp_2Mo(\eta^2\text{-}C_6H_5CHO)$ (6)	4.26, 4.71	4.51 (s, 1, CHO) 6.80–7.02 (m, 5, C_6H_5)	
$Cp_2Mo(\eta^2\text{-}H_2CO)$ (7)	4.70	3.03 (s, 2, CH_2)	1155 (ν(CO))
$Cp_2Mo(\eta^2\text{-}C_6H_5CHNC_6H_5)$ (8)	4.34, 4.43	3.14 (s, 1, CH) 6.20–7.05 (m, 10, C_6H_5)[b]	
$Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CS]$ (9)	4.31	6.70–7.60 (m, 10, C_6H_5)[d]	598 (ν(CS))
$Cp_2Mo[O_2C_2(CO_2C_2H_5)_4]$ (10)	5.69	1.26 (t, 12, J_{HH} = 7 Hz) 4.17 (q, 8, J_{HH} = 7 Hz)	1730 (ν(CO))
$Cp_2Mo[O_2C_2(CF_3)_4]$ (11)	5.57		1245, 1217, 1193 (ν(CF))
$Cp_2Mo[O_2(C(CF_3)_2)_2O]$ (12)	5.68		1225, 1196, 1185 (ν(CF))
$Cp_2Mo(O_2C_{14}H_8)$ (13)	5.54	7.08–8.60 (m, 8, $C_{14}H_8$)[e]	1055 (ν(CO))

[a] Data given as chemical shift in parts per million (multiplicity, relative intensity, assignment). Recorded at 25 °C in CD_2Cl_2 unless otherwise stated. [b] In CS_2. [c] Full width at half height 1 Hz. [d] In $CDCl_3$. [e] In THF-d_8.

(*Z*)-stilbene, enhancing the metal–ligand interaction through a better back bonding from the metal fragment to the olefin's π^* orbital.[16] There are a few cases of *Z*–*E* isomerization of a coordinated olefin in the literature.[17–21] Except for one photochemical isomerization[17] all these rearrangements occur spontaneously without any inducing agent as found in the present case.

Reactions with Heteroolefins. Reaction of the (*Z*)-stilbene complex 1 with various heteroolefinic ligands L in toluene at 40–70 °C results in the smooth elimination of free (*Z*)-stilbene and the clean formation of the substitution products Cp_2MoL, where L can be formaldehyde (7), nonenolizable ketones (3–6), benzalanilide (8), and thiobenzophenone (9) (eq 2). Though the reaction time



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	3	4	5	6	7	8	9
X	O	O	O	O	O	NC_6H_5	S
R	CF_3	CO_2CH_3	C_6H_5	H	H	H	C_6H_5
R'	C_6H_5	C_6H_5	C_6H_5	C_6H_5	H	C_6H_5	C_6H_5

strongly depends on the nature of the incoming ligand, the reaction is usually complete within 6 h and the yields are good. All products have been isolated as analytically pure crystals after chromatographic workup and characterized by spectroscopic methods (^{1}H NMR, IR, electron-impact mass spectrometry) (Tables I and II). The common structure of a bent metallocene complex with side-on bonded heteroolefin ligand RR'C=X is concluded particularly by the lack of the intense ν(C=X) vibration of the ligand system upon coordination to the Cp_2Mo fragment. In favorable cases, the corresponding band in the

Table II. Analytical and Mass Spectral Data

compound	anal.[a] C	anal.[a] H	mol[b]
$Cp_2Mo[\eta^2\text{-}(E)\text{-}C_6H_5CHCHC_6H_5]$ (2)	70.65 (70.93)	5.48 (5.46)	408
$Cp_2Mo(\eta^2\text{-}C_6H_5COCF_3)$ (3)	53.97 (54.01)	3.80 (3.78)	402
$Cp_2Mo(\eta^2\text{-}C_6H_5COCO_2CH_3)$ (4)	58.29 (58.47)	4.65 (4.63)	392
$Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CO]$ (5)	67.39 (67.65)	4.84 (4.94)	410
$Cp_2Mo(\eta^2\text{-}C_6H_5CHO)$ (6)	61.20 (61.45)	4.73 (4.94)	334
$Cp_2Mo(\eta^2\text{-}H_2CO)$ (7)	51.41 (51.58)	4.82 (4.72)	258
$Cp_2Mo(\eta^2\text{-}C_6H_5CHNC_6H_5)$ (8)	67.55 (67.81)	5.23 (5.20)	409
$Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CS]$ (9)	64.98 (65.09)	4.67 (4.75)	426
$Cp_2Mo[O_2C_2(CO_2C_2H_5)_4]$ (10)	50.06 (50.18)	5.29 (5.26)	576[c]
$Cp_2Mo[O_2C_2(CF_3)_4]$ (11)	34.33 (34.43)	1.82 (1.81)	560
$Cp_2Mo[O_2C_2(C(CF_3)_2)_2O]$ (12)	33.46 (33.47)	1.84 (1.76)	576
$Cp_2Mo(O_2C_{14}H_8)$ (13)	66.19 (66.37)	4.28 (4.18)	436

[a] Calculated values in parentheses. [b] Determined by electron impact mass spectrometry. [c] Registered by field desorption mass spectrometry; highest peak in electron-impact mass spectrum: *m/z* 271 ($C_2(CO_2C_2H_5)_3CO^+$).

complex can be detected: the shift $\Delta\nu$ observed for ν(C=O) of formaldehyde in 7 is 591 cm^{-1} and for ν(C=S) of thiobenzophenone in 9 is 660 cm^{-1}. These values obviously reflect a strong back bonding from the metal to the unsaturated organic ligand.

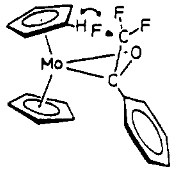
In the case of the benzalanilide complex $Cp_2Mo(\eta^2\text{-}C_6H_5CHNC_6H_5)$ (8) where such a straightforward interpretation on the basis of IR spectral data is not possible, a single-crystal X-ray structural analysis has confirmed the proposed structure with a side-on bonded imine unit via both the nitrogen and carbon atoms.[22]

The room-temperature ^{1}H spectrum of the 1,1,1-trifluoroacetophenone adduct 3 shows as expected two distinct singlets for the two inequivalent Cp rings; however,

(16) Ittel, S. D.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *74*, 121.
(17) Schenck, G. O.; Koerner von Gustorf, E.; Jun, M.-J. *Tetrahedron Lett.* **1962**, 1059.
(18) Ashley-Smith, J.; Green, M.; Wood, D. C. *J. Chem. Soc. A* **1970**, 1847.
(19) Chicote, M. T.; Green, M.; Spencer, J. L.; Stone, F. G. A.; Vincente, J. *J. Organomet. Chem.* **1977**, *137*, C8.
(20) (a) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046. (b) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282.
(21) Edwards, B. H.; Rogers, R. D.; Sikora, D. J.; Atwood, J. L.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 416.

(22) Okuda, J.; Herberich, G. E.; Raabe, E.; Bernal, I. manuscript in preparation. The structure of a Pt complex bearing side-on bonded imine has been reported, cf. ref 31.

one of them is significantly broadened in comparison with the other (full width at half height 1 Hz vs. 0.3 Hz). Since this broadening is temperature independent in the range of 50 to −80 °C, we assume it to be caused by a through-space coupling of the Cp protons with the three fluorine atoms of the CF_3 group.[23]



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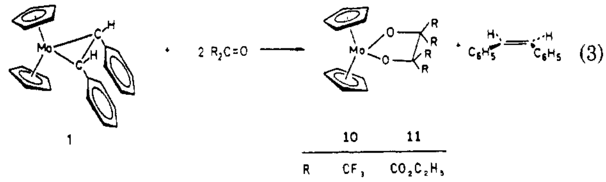
The benzophenone complex $Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CO]$ (**5**), though isolable as crystalline material, appears to be quite reactive in solution. Apparently the ketone ligand in **5** is somewhat less firmly bonded to the Cp_2Mo moiety due to intramolecular steric crowding similar to the situation found in the (*Z*)-stilbene complex **1**. **5** is therefore susceptible to ligand replacement reactions, e.g. with acetylenes and carbon disulfide, at temperatures between 50 and 60 °C. It is noteworthy in this connection that the thiobenzophenone complex $Cp_2Mo[\eta^2\text{-}(C_6H_5)_2CS)]$ (**9**) is much more stable than **5** and does not undergo substitution of thiobenzophenone with other acceptors under the same conditions.

Ligand systems which have enolizable functionalities such as CH_3CO (acetaldehyde, acetone, 1,1,1-trifluoroacetone, acetophenone, methyl pyruvate) induce the above mentioned *Z–E* isomerization of the coordinated (*Z*)-stilbene in **1** and cannot be coordinated to the molybdenocene fragment using **1**.

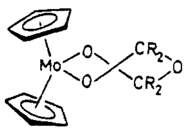
The reaction of monomeric formaldehyde or paraformaldehyde with **1** is essentially also a substitution reaction to give the thermally robust formaldehyde complex $Cp_2Mo(\eta^2\text{-}H_2CO)$ (**7**), but the (*E*)-stilbene complex **2** is formed as a side product in variable yields. Best yields of **7** are achieved when **1** is reacted in tetrahydrofuran (THF) with dried paraformaldehyde at 40 °C over a period of 2 days. **7** is now available by two different methods in better yields[12,24] and has been also subject of an X-ray crystallographic study of which the results fully confirm the structure of a molybdenocene complex with a side-on bonded formaldehyde ligand.[24] Very careful mass spectrometric analysis of this formaldehyde complex has revealed that neither the CH bond (to give under decarbonylation molybdenocene dihydride[25a]) nor the CO bond of the coordinated formaldehyde (to give molybdenocene oxide $Cp_2Mo{=}O$ and methylene CH_2[26a]) can be broken.[27] So far we have not been able to find any reaction during which the formaldehyde remains complexed to the molybdenum center.[28]

Oxidative Coupling Reactions. The extremely electrophilic ketones diethyl ketomalonate (DEKM) and hexafluoroacetone (HFA) react with **1** to give not the expected 1:1 adducts but instead diolate complexes **10** and **11** derived from oxidative coupling of two ketone molecules (eq 3). While **1** is slowly isomerized by DEKM to **2** in



THF at room temperature, the conversion to complex **10** dominates above 40 °C. Thermally stable, mauve crystals can be isolated in high yield and all spectroscopic data are consistent with the structure of a tetravalent molybdenum diolate complex. A very similar titanium compound, $Cp_2Ti[O_2C_2(CO_2C_2H_5)_4]$, has been prepared from $Cp_2Ti(CO)_2$ and DEKM and the head-to-head coupling of the two ketone units confirmed by X-ray structure.[29]

The reaction of **1** with HFA is very vigorous even at −100 °C. Chromatographic workup of the resulting mixture gives the diolate complex **11** as brown crystals in good yield besides a second product **12**. **11** has been fully characterized by analysis and spectroscopic means; especially the ^{19}F NMR spectrum exhibits one sharp signal at −66.8 ppm for all four equivalent CF_3 groups confirming the presence of a perfluoropinacolate ligand. Perfluoropinacolate complexes are very scarce in the literature and, to our knowledge, have never been formed directly from two HFA units at a transition-metal center.[30] The side product of this reaction, **12**, is proposed to have the structure of a metallatrioxane derivative. The six-membered ring can be inferred from the NMR spectra: Both the ^1H and ^{19}F NMR spectra show one sharp signal at −80 °C. The source for the additional oxygen is probably adventitious traces of air or moisture.



(R = CF_3)

12

Since we have no evidence for the intermediate formation of a 1:1 adduct during the reaction of **1** with DEKM and HFA, we suggest a different pathway for the formation of the diolate complexes as has been proposed in the numerous cases where HFA is head-to-tail coupled at zerovalent nickel metal centers.[31] Although steric requirements are definitely responsible for the exclusive head-to-head coupling,[32] a dipolar or diradical intermediate accounts also for this reaction which selectively takes place with DEKM and HFA. Experiments conducted to trap some intermediate species, e.g. by performing the reaction of **1** with the electrophilic ketones in the presence of other ligands L or using only half equivalent of DEKM or HFA, remained so far fruitless. Isolable 1:1 adducts **3–7** did not

(23) For a similar case, cf. Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1969**, 2215.

(24) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

(25) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Berke, H.; Bankhardt, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754. Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (d) Buhro, W. E.; Georgiu, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

(26) (a) Kropp, K.; Skribbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690.

(27) Okuda, J.; Herberich, G. E.; Müller, J., unpublished results.

(28) Protonolysis with trifluoroacetic acid affords $Cp_2Mo(O_2CCF_3)_2$ quantitatively, but in the mixture only methanol could be identified.

(29) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349.

(30) (a) Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 96. (b) Cripps, W. S.; Willis, C. J. *Can. J. Chem.* **1975**, *53*, 809.

(31) Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551.

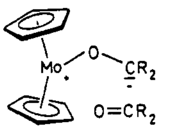
(32) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

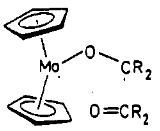
Table III. Cyclic Voltammetric Data for Oxidation of $Cp_2Mo(O_2C_{14}H_8)$ (13)[a]

	E_p^{ox}, V	E_p^{red}, V	$E_{1/2}$,[b] V	i_{ox}/i_{red}
$13^0/13^+$	+0.04	−0.02	+0.01	1.00
$13^+/13^{2+}$	+0.88	+0.82	+0.85	1.00

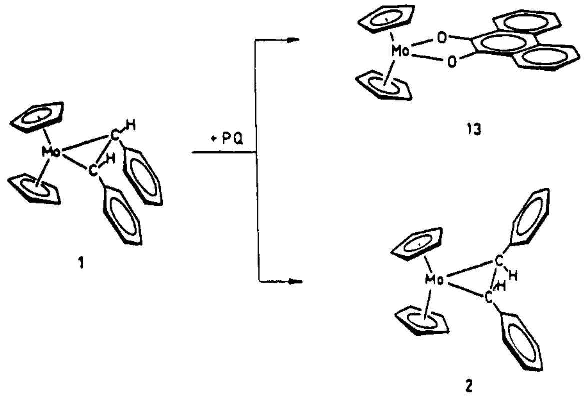
[a] Registered in referenced containing 0.1 M Bu_4NPF_3 with a scan rate of 200 mV/s at 20 °C. [b] Potentials are referenced to calomel electrode containing a saturated NaCl solution.

give mixed diolate derivatives either, but again formed **10** and **11**.





When 1 equiv of 9,10-phenanthrenequinone (PQ) is reacted with **1** in toluene at room temperature, an approximately 1:1 mixture consisting of the (*E*)-stilbene complex **2** and the enediolate complex of molybdenocene $Cp_2Mo(O_2C_{14}H_8)$ (**13**) is obtained within 15 min (eq 4). Similar reaction occurs with benzil leading to the enediolate complex $Cp_2Mo[O_2C_2(C_6H_5)_2]$ briefly mentioned by Nakamura.[33] The homologous tungstenocene derivative of **13**, $Cp_2W(O_2C_{14}H_8)$, had been prepared by Green et al.[34]



(4)

Analytical and spectroscopic data of **13** are consistent with the structure containing a molybdenum(IV) center coordinated to a 9,10-phenanthrenediolate ligand. The cyclovoltammogram exhibits two completely reversible oxidation steps in CH_2Cl_2, formally corresponding to the formation of molybdenum(V) and -(VI) species (Table III).[35] This electrochemical behavior is typical for a metal complex bearing an extensively delocalized ligand system such as quinones.[36]

Conclusion

Some general trends concerning the reactivity of the (*Z*)-stilbene complex **1** in comparison to other bent metallocene systems can be extracted from the results of the present study which has demonstrated a broad spectrum of reactivity of **1** depending on the nature of the ligand L. Low-valent molybdenocene complexes of the type Cp_2MoL are obtained by ligand displacement reaction when substrates with good electron-withdrawing ability such as acetylenes,[10] activated olefins, heteroolefins, and heteroallenes[14] are reacted with **1**. Strongly activated ketones DEKM and HFA as well as 1,2-diones oxidize the d^4 metal center affording complexes containing Cp_2Mo^{2+} units. Very strong π-acceptor molecules at lower temperatures and protic substances cause the *Z*–*E* isomerization to give the (*E*)-stilbene complex **2**. The first step of both the substitution and the *Z*–*E* isomerization is probably a single electron transfer[37] from the electron-rich metal center of **1** to the acceptor molecule to give an intermediate which is either stabilized as the (*E*)-stilbene complex **2** or which is converted under replacement of the (*Z*)-stilbene ligand by a ligand L to the low-valent complexes of the type Cp_2MoL. Apparently a very fine balance of electronic and steric properties of L as well as reaction temperature is responsible for the outcome of the reaction. However, the (*Z*)-stilbene complex **1** can in fact serve in many cases as a convenient synthetic source for the low-valent Cp_2Mo fragment.

The ligand substitution reaction of **1** parallels the addition of organic π-acceptor molecules to the 15-electron vanadocene Cp_2V, giving rise to complexes of the type Cp_2VL, where L can be formaldehyde,[25c] dimethyl fumarate,[20] dimethyl acetylenedicarboxylate,[20] thiobenzophenone,[38] and heteroallenes such as carbon disulfide.[39] There exists obviously a very close structural analogy to the corresponding molybdenocene complexes.[24] On the other hand, the oxidative coupling reaction of the electrophilic ketones and 1,2-diones indicate a certain electronic flexibility of the d^4 metal center in **1**, as documented by the clean formation of molybdenum(IV) complexes **10**–**13**. This latter behavior ressembles the reaction of low-valent titanocene, e.g. in the form of its dicarbonyl $Cp_2Ti(CO)_2$[40] or its bis(trimethylphosphine) complex $Cp_2Ti(PMe_3)_2$[41] for which an oxidation reaction with organic π-acceptors to give titanium(IV) derivatives is rather common.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. THF, diethyl ether, and toluene were distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation from sodium/potassium alloy. CH_2Cl_2 was distilled from CaH_2. NMR solvents were degassed by freeze–pump–thaw cycles on a vacuum line prior to use. $Cp_2Mo[\eta^2\text{-}(Z)\text{-}C_6H_5CH{=}CHC_6H_5]$ (**1**)[10] and thiobenzophenone[42] were prepared by published methods. All other reagents were purchased from commercial sources and used as received. Chromatography was carried out under nitrogen with alumina columns (Woelm, N-Super-O; deactivated with 7% water) made up in pentane.

^1H NMR spectra were recorded on a JEOL NM-C-60 HL spectrometer; ^{13}C and ^{19}F NMR spectra were measured on a Bruker WP 80 SY instrument. ^1H and ^{13}C NMR chemical shifts are referenced to internal Me_4Si; ^{19}F NMR are referenced to internal $CFCl_3$. IR spectra were obtained on a Perkin-Elmer 580 IR spectrometer using KBr pellets and calibrated with polystyrene film. Electron impact mass spectra were recorded at 70 eV on a Varian MAT CH-5-DF mass spectrometer. Melting points were

(33) Nakamura, A. *J. Organomet. Chem.* **1979**, *164*, 183.
(34) Gore, E.; Green, M. L. H.; Harriss, M. G.; Lindsell, W. E.; Shaw, H. *J. Chem. Soc. A* **1969**, 1981.
(35) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.
(36) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.
(37) Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic: New York, 1978.
(38) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 841.
(39) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**. 1612. (b) Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165. (c) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173.
(40) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297.
(41) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem.* **1985**, *97*, 425; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.
(42) Scheeren, J. W.; Ooms, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149.

determined in capillary tubes under nitrogen and are uncorrected. Elemental analyses were performed by Analytische Laboratorien, D-5250 Engelskirchen, West Germany.

$Cp_2Mo[\eta^2$-(*E*)-$C_6H_5CH{=}CHC_6H_5]$ (2). To a solution of 1 (400 mg, 0.98 mmol) in CH_2Cl_2 (10 mL) was added maleic anhydride (10 mg, 0.1 mmol), and the mixture was stirred for 0.5 h at room temperature. The solvent was removed under reduced pressure and the residue chromatographed (2 × 20 cm). Elution with hexane/CH_2Cl_2 (1:1) gave a brownish orange band. Evaporation of the solvent and recrystallization from pentane/CH_2Cl_2 afforded 2 as light brown crystals (300–350 mg, 75–88%); mp 145 °C, dec above 190 °C. ^{13}C NMR (C_6D_6): δ 153.1 (s, C_{ipso}), 128.0, 127.8, 123.1, (d, C_6H_5), 84.1 (d, $^1J_{CH}$ = 178 Hz, C_5H_5), 32.4 (d, $^1J_{CH}$ = 142 Hz, =CH).

$Cp_2Mo(\eta^2$-$C_6H_5COCF_3)$ (3). To a solution of 1 (1.22 g, 3.0 mmol) in THF (15 mL) was added 1,1,1-trifluoroacetophenone (410 μL, 523 mg, 3.0 mmol). After the mixture was stirred for 6 h at 50 °C, the solvent was removed in vacuo and the residue chromatographed (2 × 20 cm). With pentane as an eluent (*Z*)-stilbene and unreacted ketone were eluted. Further elution with hexane/CH_2Cl_2 (1:1) gave an orange-red band. The orange eluate was concentrated and cooled to −20 °C. Recrystallization from pure CH_2Cl_2 afforded 3 as orange flakes (530 mg, 44 %); mp 181 °C dec. ^{19}F NMR ($CDCl_3$): δ −60.1 (s).

$Cp_2Mo(\eta^2$-$C_6H_5COCO_2CH_3)$ (4). A mixture of 1 (1.0 g, 2.5 mmol) and methyl benzoylformate (700 μL, 807 mg, 4.92 mmol) in toluene (15 mL) was stirred for 6 h at 50 °C. After the solvent was removed in vacuo, the residue was chromatographed on alumina (2 × 20 cm). (*Z*)-Stilbene was first removed with pentane and then elution with hexane/CH_2Cl_2 gave a broad pink band which was collected. The solution was concentrated under reduced pressure and hexane was added to give a red solid. Recrystallization from hexane/CH_2Cl_2 yielded 4 as dark red cubes (500 mg, 52 %); mp 189 °C dec.

$Cp_2Mo[\eta^2$-$(C_6H_5)_2CO]$ (5). Benzophenone (730 mg, 4.0 mmol) was dissolved in a solution of 1 (820 mg, 2.02 mmol) in THF (20 mL). After the solution was stirred overnight at 50 °C, the solvent was removed in vacuo and the residue chromatographed (2 × 30 cm). Excess benzophenone and (*Z*)-stilbene were eluted with pentane and a brownish orange band was eluted with pentane/CH_2Cl_2 (3:1) which was shown to contain 2 (50–60 mg). On elution with pentane/CH_2Cl_2 a yellow band which contained traces of Cp_2MoH_2 was removed. Further elution with CH_2Cl_2 gave a broad pink band which was collected as a bright orange solution. The solvent was evaporated and the residue repeatedly recrystallized from hexane/CH_2Cl_2 to afford 450 mg (55%) of 5 as orange needles; mp 189 °C dec.

$Cp_2Mo(\eta^2$-$C_6H_5CHO)$ (6). To a solution of 1 (2.0 g, 4.92 mmol) in toluene (30 mL) was added 1 mL of benzaldehyde (1.04 g, 9.8 mmol) and the mixture stirred overnight at 50 °C. The solvent was evaporated in vacuo and the residue chromatographed (2 × 20 cm). (*Z*)-Stilbene and excess benzaldehyde were eluted with hexane/CH_2Cl_2 (4:1), then elution with hexane/CH_2Cl_2 (1:10) gave a brownish orange band which was collected. After removal of the solvent the brown powder was again chromatographed. Upon elution with hexane/ether/CH_2Cl_2 (75:23:2) an orange band was obtained. Concentration and cooling to −20 °C yielded 500 mg of extremely air-sensitive pale brown flakes (30%); mp 170 °C dec.

$Cp_2Mo(\eta^2$-$H_2CO)$ (7). To a solution of 1 (1.0 g, 2.5 mmol) in THF (15 mL) was added paraformaldehyde (3.75 g, 125 mmol) and the suspension vigorously stirred at 35 °C for 3.5 days. The solvent was removed in vacuo and the residue chromatographed (2 × 20 cm). Elution with pentane gave (*Z*)-stilbene and then, with hexane/CH_2Cl_2 (1:1) a brownish orange band of 2 (50–100 mg). Further elution with CH_2Cl_2/THF (4:1) gave an intense orange band which was collected. Recrystallization from hexane/CH_2Cl_2 gave 7 as orange-yellow platelets (120–180 mg, 19–28%); mp 179 °C dec. ^{13}C NMR ($CDCl_3$): δ 86.8 (d, $^1J_{CH}$ = 179 Hz, C_5H_5), 44.9 (t, $^1J_{CH}$ = 167 Hz, CH_2).

$Cp_2Mo(\eta^2$-$C_6H_5CHNC_6H_5]$ (8). A solution of 1 (800 mg, 1.97 mmol) and *N*-benzalaniline (700 mg, 3.96 mol) in toluene (15 mL) was stirred for 16 h at 40 °C. The solvent was removed in vacuo and the residue chromatographed (2 × 20 cm). Excess imine and (*Z*)-stilbene were eluted with pentane. Elution with hexane/CH_2Cl_2 (9:1) gave a pale brown band which was collected. After removal of the solvent the oily residue was chromatographed again as above. Recrystallization of the yellow powder from hexane/CH_2Cl_2 gave dark red prisms of 8 (270 mg, 33%); mp 146 °C dec.

$Cp_2Mo[\eta^2$-$(C_6H_5)_2CS]$ (9). Thiobenzophenone (650 mg, 3.28 mmol) was added to a solution of 1 (1.3 g, 3.2 mmol) in THF (20 mL) and the green solution stirred for 6 h at 50 °C. After evaporation of the solvent under vacuum, the residue was chromatographed (2 × 20 cm). Elution with pentane removed excess thiobenzophenone and (*Z*)-stilbene as a blue band and elution with hexane/CH_2Cl_2 (1:2) gave a brownish orange band which was collected. The solvent was removed in vacuo and repeated recrystallization from CH_2Cl_2 afforded 9 as dark red needles (710 mg, 52%); mp 245 °C dec.

$Cp_2Mo[O_2C_2(CO_2C_2H_5)_4]$ (10). A mixture of 1 (1.22 g, 3.0 mmol) and diethyl ketomalonate (1 mL, 1.1 g, 6.32 mmol) was heated at 60 °C for 6 h. When the solution cooled to room temperature, violet needles precipitated which were filtered and washed with pentane. The mother liquor was concentrated and chromatographed (2 × 20 cm). Elution with hexane gave (*Z*)-stilbene and then a brown band separated with hexane/CH_2Cl_2 (1:1) which was shown to contain traces of 2. Further elution with CH_2Cl_2/THF/EtOH (90:5:5) gave a pink band which after evaporation of the solvent was combined with the precipitate; recrystallization from THF afforded 10 as mauve needles (1.1 g, 64 %); mp 186 °C dec.

$Cp_2Mo[O_2C_2(CF_3)_4]$ (11) and $Cp_2Mo[O_2(C(CF_3)_2)_2O]$ (12). Through a solution of 1 (450 mg, 1.11 mmol) in THF (10 mL) was passed gaseous hexafluoroacetone for 1 min at 0 °C. The solution was filtered, the filtrate evaporated to dryness, and the residue chromatographed (1.5 × 60 cm). Elution with pentane/CH_2Cl_2 (4:1) gave an olive green band which slowly separated from a broad purple band. The first, brown eluate gave, after removal of the solvent and recrystallization from CH_2Cl_2, 11 as brown crystals (60 mg, 9%); mp 245 °C dec. ^{19}F NMR (CD_2Cl_2, −80 °C): δ 79.8 (s). The second band yielded a bright purple eluate which after evaporation of the solvent and recrystallization afforded 12 as violet platelets (410 mg, 67%); mp 205 °C dec. ^{19}F NMR (CD_2Cl_2): δ −66.8 (s).

$Cp_2Mo(O_2C_{14}H_8)$ (13). To a solution of 1 (900 mg, 2.21 mmol) in THF (10 mL) was added 9,10-phenanthrenequinone (520 mg, 2.5 mmol). The color of the solution turned to dark brown at room temperature within 15 min. The solvent was removed in vacuo and the residue chromatographed (2 × 20 cm). An orange band containing excess quinone and (*Z*)-stilbene was eluted with pentane. Further elution with hexane/CH_2Cl_2 (1:1) separated an orange-brown band due to 2 (250 mg). With CH_2Cl_2/acetone (10:1) as an eluent a red-brown band was eluted. Evaporation of the solvent under vacuum and recrystallization from THF/hexane afforded purple crystals of 13 (380 mg, 40 %); dec above 285 °C.

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