The Photochemistry of [$CpMo(CO)_3(\eta^1\text{-}C_3H_5)$] in Frozen Gas Matrices at 10 K and the Behaviour of [$CpMo(CO)_2(\eta^3\text{-}C_3H_5)$] Isomers in Different Media

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On photolysis of [$CpMo(CO)_3(\eta^1\text{-}C_3H_5)$] in solid inert matrices at low temperature, one CO molecule is eliminated yielding the *exo* and *endo* isomers of [$CpMo(CO)_2(\eta^3\text{-}C_3H_5)$] in almost 1:1 proportions, although the fraction of the *exo* conformer is increased by prolonged broad-band UV irradiation. If gaseous [$CpMo(CO)_2(\eta^3\text{-}C_3H_5)$] is isolated in an Ar matrix the proportions of the two conformers are again about 1:1, indicating that they possess almost equal energies, as confirmed by DFT calculations (B3LYP/SDD). This situation changes in a solvent environment, where increasing the polarity of the solvent favours the *exo* isomer, as indicated by the ratios *exo*/*endo* = 1.7:1 (pentane or cyclohexane), 3.0:1 (benzene) and 3.3:1 (CH_2Cl_2) determined by IR and NMR measurements. Such a finding is consistent with the results of DFT calculations, which reveal that the *exo* isomer is more polar.

Introduction

The dynamics of allylmolybdenum moieties have relevance not only to the formation of new C−C bonds by way of nucleophilic attack on the coordinated allyl groups,[1] but also to catalytic processes involving olefin functionalisation. One example is the oxidation of propene in the presence of a heterogeneous molybdenum oxide catalyst, a process which is believed to proceed by the trapping of allyl radicals by Mo atoms on the catalyst surface; the resulting allyl-Mo fragments are thought subsequently to undergo several shift and rearrangement reactions, finally yielding acrolein.[2] Interest in the mechanisms of this and other reactions involving allylmolybdenum fragments initiated the present investigation of the photolytic behaviour of [$CpMo(CO)_3(\eta^1\text{-}C_3H_5)$] (**1**)[3] in solid inert matrices at low temperatures.

The matrix photochemistry of the analogous tungsten compound [$CpW(CO)_3(\eta^1\text{-}C_3H_5)$] has already been examined by Rest et al.[4] They found evidence for photodecarbonylation yielding products displaying two pairs of bands in the ν(CO) region of the IR spectrum. The bands were assigned to a mixture of [$CpW(CO)_2(C_3H_5)$] isomers involving either an η^1- or an η^3-coordinated allyl group and formed in accordance with the reaction sequence set out in Figure 1. In the light of these intriguing results, it was hoped to shed more light on the fate of [$CpM(CO)_2(\eta^1\text{-}C_3H_5)$] intermediates (M = Cr, Mo, W) generated through photodecarbonylation by investigation of the corresponding molybdenum compound. These new spectroscopic studies were to be supported by quantum mechanical calculations focussed on the proposed products of the changes.

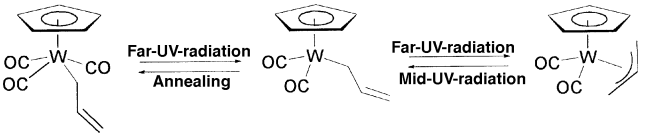

Figure 1. Proposed photochemistry of [$CpW(CO)_3(\eta^1\text{-}C_3H_5)$] in solid CH_4, Ar, N_2, or CO matrices[4]

Results and Discussion

Photolysis of 1 in Low Temperature Matrices

The vapour of **1** was co-condensed with an excess of argon on a CsI window at 10 K. The IR spectrum of the resulting matrix showed three (matrix-split) bands in the ν(CO) region characteristic of the molecule [$CpMo(CO)_3(\eta^1\text{-}C_3H_5)$] [Figure 2(a)]. Photolysis of the matrix with light having wavelengths near 369 or 313 nm or with broad-band UV light resulted in the quantitative decomposition of the starting material and gave rise to two pairs of bands (which will subsequently be referred to as "doublets") of almost equal intensity in the ν(CO) region of the IR spectrum (one at 1966/1891 cm^{-1} and the other at 1974/1907 cm^{-1}), together with a band near 2140 cm^{-1} due to free CO. The results are thus very similar to those observed previously in the case of the tungsten compound.[4] Furthermore, as with the tungsten system, prolonged photolysis caused one set of bands to grow somewhat in intensity at the expense of the other set. This immediately prompted the impression that molybdenum follows tungsten in the formation of two species of the type [$CpM(CO)_2(C_3H_5)$] (M = Mo or W) with η^1- and η^3-coordinated allyl groups, respectively. It seems very surprising, however, that photolysis of both the molybdenum and tungsten compounds gives rise to 16- and 18-electron species [$CpM(CO)_2(C_3H_5)$] in almost equal proportions, when the

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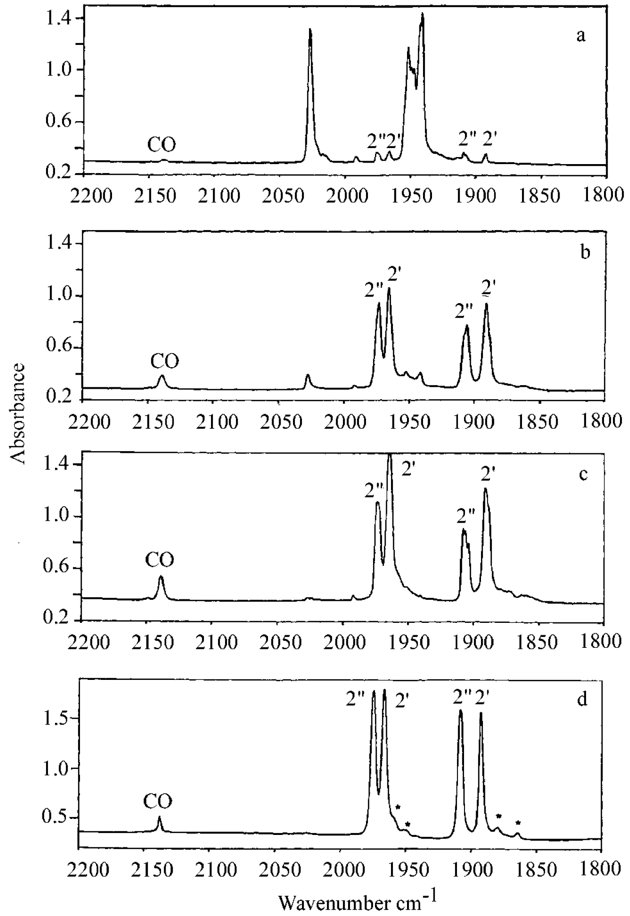

Figure 2. IR absorption spectrum in the region 2200–1800 cm^{-1} displayed by a solid Ar matrix containing [CpMo(CO)$_3$(η^1-C$_3$H$_5$)] at 10 K (a); showing the effects of photolysis with broad-band UV radiation for 10 min (b); and of prolonged photolysis (c); trace (d) shows the spectrum of [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] isolated in an Ar matrix at 10 K; bands marked with an asterisk arise from [CpMo(^{12}CO)(^{13}CO)(η^3-C$_3$H$_5$)] present in natural abundance

16-electron compound is likely to be much less stable than the 18-electron one.

In order to shed more light on this finding, the compound [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (**2**)[3] was isolated in an argon matrix [Figure 2(d), Table 1]. Although this material contains only η^3-allyl groups, the IR spectrum of the matrix-isolated vapour showed the same two sets of doublets as did the spectrum of the matrix after photolysis of **1**. Moreover, the two doublet absorptions exhibited by the IR spectrum of **2** were observed to be almost exactly equal in intensity. It seems unlikely that [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] rearranges in the gas phase *en route* to the cold window to the 16-electron compound [CpMo(CO)$_2$(η^1-C$_3$H$_5$)], with which it then co-exists in equilibrium. This finding is therefore at odds with an assignment of one of the doublets to a 16-electron compound of Mo or W, and accordingly the real origin of the extra bands has still to be unravelled.

One possible explanation for the observation of a multiplet instead of a single band is so-called "matrix splitting" caused by the residence of trapped species in different matrix sites.[5] However, the doublet splitting observed for **2** isolated in an argon matrix would be rather large (8 and 16 cm^{-1}), and the possibility of matrix splitting can be more or less excluded by the results of experiments with different matrices, for example Kr, CH$_4$ and CO, in which **2** continued to show two ν(CO) doublets of roughly equal intensity. Changing the matrix normally alters or eliminates any splitting that depends on the character of the solid host. Therefore the two doublets must belong to different dicarbonyl isomers, both bearing η^3-bonded allyl ligands. These are designated **2**′ and **2**′′ in the following text.

Table 1. IR spectrum of a solid Ar matrix doped with [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (**2**) at ca. 10 K in the region 2400–650 cm^{-1}

Wavenumber (cm^{-1})	likely assignment
1974	ν(CO)/**2**′′
1966	ν(CO)/**2**′
1907	ν(CO)/**2**′′
1891	ν(CO)/**2**′
1490	δ(CH$_2$)$_{as}$/allyl
1462	δ(CH$_2$)$_s$/allyl
1432	ν(CC)/Cp
1422	ν(CC)/Cp
1228	π(CH)/allyl
1015	β(CH)/Cp
1011	β(CH)/Cp
889	ρ$_w$(CH$_2$)$_s$/allyl
885	α(CH)/Cp
808	γ(CH)/Cp
803	γ(CH)/Cp
745	?

Dynamic Behaviour of 2 in Solution

High- and low-temperature NMR studies had suggested previously[6] that **2** enters into a conformational equilibrium in solution. There are two conformers, which can be interconverted by *formal* rotation of the η^3-allyl group [**2A** (allyl rotation angle θ = 180°) and **2B** (θ = 0°) in Figure 3]. Apart from a simple rotation of the allyl group, there are in general four possible mechanisms that might explain the dynamic behaviour of allyl groups bound to metal centres:[6–9]

(i) The olefin rotation mechanism involves an intermediate with the C^1 and C^2 atoms of the allyl group remaining bonded to the metal while rotation proceeds around the C^2–C^3 axis.

(ii) Alternatively, the C^1 and C^3 atoms in the intermediate can remain coordinated while C^2 flips from one side to the other.

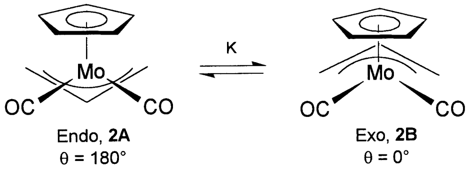

Figure 3. Conformational isomers of [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (**2**) in solution and their allyl rotation angle θ relative to the carbonyl ligands

(iii) In the π-σ-π mechanism, the intermediate contains an η^1-bonded allyl group which can freely rotate around the C^1−C^2 axis.
(iv) There is also the possibility that the isomers are interconverted by a kind of pseudorotation reflecting the nonrigidity of the parent ligand-metal framework.

Mechanism (iii) is commonly accepted to operate, for instance, for compounds of the type [CpMoI(NO)(η^3-C$_3$H$_5$)],[10,11] while NMR spectroscopic investigations[6] led Faller et al. to propose mechanism (iv) for **2**. The ^{1}H NMR spectra of the two individual conformers of **2** (in solution in [D$_6$]benzene) can be observed independently as broad signals at ambient temperatures, the relative intensities of the signals implying an equilibrium constant *K* of 3.0 at 5 °C. The two sets of resonances coalesce at 86 °C. Whatever mechanism is responsible for the isomerisation, the change is slow on the NMR timescale, with an activation barrier estimated to be 51.5 kJ/mol.[6] Compound **2** crystallises from solution with the η^3-allyl ligand in the preferred *exo* conformation (isomer **2B**).[10] Thus, the *endo*-*exo* equilibrium adjusts the solution concentrations as the *exo*-form crystallises. It follows that evaporation of the solvent affords only the *exo* conformer **2B**. Previous reports of the IR spectrum of **2** in solution referred to the presence of two doublets in the ν(CO) region,[12] and these too have been rationalised on the assumption of a conformational equilibrium between **2A** and **2B**.[13,14]

Isomerism of 2 in Low Temperature Matrices and Quantum Mechanical Calculations

Bearing all these findings in mind, it is tempting to identify the species **2′** and **2′′** observed after quenching the vapour of **2** with a large excess of matrix gas at 10 K with the two conformers **2B** and **2A**, respectively. According to the NMR results for solutions, **2A** and **2B** must then be present in the gas phase. To test this conclusion, further experiments were performed.

Rest et al. have reported that the three species present after photolysis of matrices containing [CpW(CO)$_3$(η^1-C$_3$H$_5$)] (see Figure 1) are all interconvertible, so that, for instance, the photolysis of the W(CO)$_2$ compounds regenerated the W(CO)$_3$ compound.[4,15] When **2** was isolated in a solid carbon monoxide matrix, however, it could not be converted into **1** either by photolysis with light of various wavelengths or by annealing, indicating that the η^3-allyl ligand is resistant to changing the mode of its ligation {unlike the one in [Co(CO)$_3$(η^3-C$_3$H$_5$)], which reacts to give [Co(CO)$_4$(η^1-C$_3$H$_5$)] in the presence of CO on photolysis}.[15b] On the other hand, compound **1** could be converted quantitatively into **2** in a carbon monoxide matrix by photolysis with broad-band UV light for 1 h. The CO ejection thus seems to be followed by a very rapid, irreversible η^1-η^3 ligation change, as suggested previously for [Re(CO)$_5$(η^1-C$_7$H$_7$)].[15d]

In all the matrices studied, the proportions of **2′** and **2′′** could be varied by broad-band UV photolysis, the ν(CO) bands at 1966 and 1891 cm^{-1} belonging to **2′** increasing at the expense of those at 1974 and 1907 cm^{-1} belonging to **2′′**.

These results may be summarised as follows: UV photolysis of **1** isolated in an Ar matrix results in the loss of one CO ligand, possibly to produce first the 16-electron product [CpMo(CO)$_2$(η^1-C$_3$H$_5$)] **2C** (see Figure 4), which is not observed since it isomerises rapidly to give the two (η^3-C$_3$H$_5$)Mo conformers **2′** and **2′′** in almost equal proportions. The two different sets of ν(CO) bands characterising **2′** and **2′′** are also observed, again with roughly equal intensity, after quenching the vapour of **2** initially at room temperature with a large excess of matrix gas at 10 K. Compounds **2′** and **2′′** must therefore also be present in the vapour of **2**.

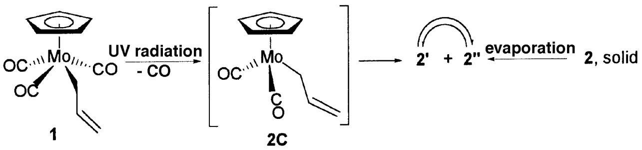

Figure 4. Proposed mechanism for the photochemistry of **1** in low temperature matrices

If energy is conveyed to such a matrix in the form of UV light (photolysis), isomer interconversion proceeds and the proportions of the two forms change in favour of what seems to be the more stable species **2′**. It has to be emphasised at this stage that the rigidity of the solid matrices at 10 K does not allow the system to reach the equilibrium state that might be anticipated for this temperature. If a π-σ-π mechanism was in operation, it would involve an intermediate **2C**. On photo-inducement of the isomerisation, however, even in the presence of an excess of CO, such an intermediate **2C** cannot revert to **1**, since the experimental results show that this is highly photolabile. The experimental results are unable therefore to argue for or against such a mechanism. On the other hand, it is possible that photoexcitation raises an electron from the low-lying HOMO (the Mo-allyl π-bonding orbital[16]) to the LUMO (the Mo-allyl π-antibonding orbital[16]). This would weaken the Mo-allyl π-bond, while the σ bond remains intact, and the allyl ligand would then be able to rotate more freely, whereas the barrier to this change is too large to be overcome by modest thermal activation of the electronic ground state.[17] A photo-isomerisation process, which has been observed previously for matrix-isolated metal *carbene* complexes,[18] is similar to the one found for **2** in that occupation of an antibonding orbital in the photo-excited state there allows free rotation around a bond, which is a rigid multiple bond in the ground state.

There is no reason therefore to question the identification of **2′** and **2′′** with **2B** and **2A**, respectively, and in order to obtain more information about these species, we set out to calculate their structures on the basis of density functional theory (B3LYP/SDD). The optimised geometries are shown

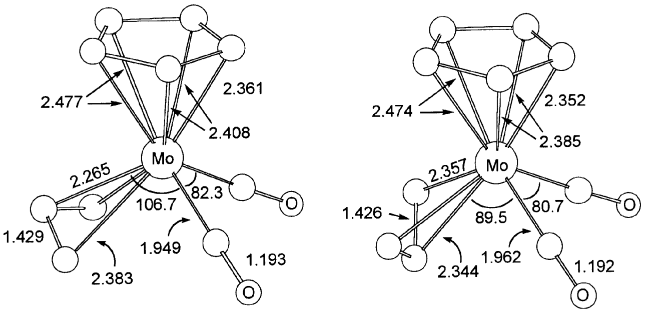

Figure 5. Structures of **2A** and **2B** as optimized by DFT calculations (B3LYP/SDD); for comparison, selected bond lengths and angles found[10] in the crystal structure of **2B** are: $Mo-C_{meso}$ 2.236(4), $Mo-C_t$ 2.359, Mo−CO 1.951(3), $Mo-C_{Cp}$ 2.321(4)-2.348(6) Å; OC−Mo−CO 82.5(2), $OC-Mo-C_{meso}$ 105.0(1)°

in Figure 5, which thus provides for the first time structural information about the *endo* conformer **2A**. The results obtained for the *exo* conformer **2B** can on the other hand be compared directly with the solid state structure.[10] As can be seen, the deviations are not unreasonable considering that theory predicts the geometry of the molecule in the gas phase, while intermolecular interactions and packing forces influence the solid state structure. Regarding the vibrational frequencies calculated for the two species, it turns out that **2B**, which had been found to be more stable in solution,[6] is indeed predicted to show a ν(CO) doublet at lower frequencies as compared with the corresponding features of **2A**. This matches the finding that the low frequency doublet observed in the matrix experiments also belongs to the more stable species **2′**. The calculations also indicate that the IR intensities of the ν(CO) modes of **2A** are very similar to those of **2B**.

It should be noted, though, that according to the NMR measurements we performed with CD_2Cl_2 as the solvent the ratio **2B**/**2A** (i.e. K in Figure 3) amounts to ca. 3.3:1 (in line with the value of $K = 3.0$ derived from previous results for a benzene solution at 5 °C[6]). At first sight, this might appear to clash with the almost equal proportions of **2′** and **2″** implied by the nearly equal intensity of the two sets of carbonyl bands observed in the IR spectrum of **2** after matrix isolation of its vapour (see Figure 2d). Such a 1:1 intensity ratio has previously been reported for the IR spectrum of **2** in cyclohexane solution,[12–14] with the inference (based on the assumption of very similar extinction coefficients) that the equilibrium constant K is close to 1 at room temperature.[14] The rather large differences between K as deduced from the ν(CO) bands in the IR and K as deduced from the ^1H NMR spectrum were ascribed to solvent effects,[14] since different solvents had been used for the two sets of measurements [the splitting of the ν(CO) bands can be resolved only for solutions in non-polar solvents]. In order to check this explanation, we recorded a ^1H NMR spectrum of **2** in $[D_{12}]$cyclohexane solution and so concluded that $K = 1.7$ and not 1.0 at 15 °C! Careful reinvestigation of the IR spectrum of **2** in cyclohexane and pentane solutions then revealed that the *exo* bands (unlike those in the matrix spectra) are much broader than the *endo* bands (see Figure 6), and *integration* of the band areas (as opposed to

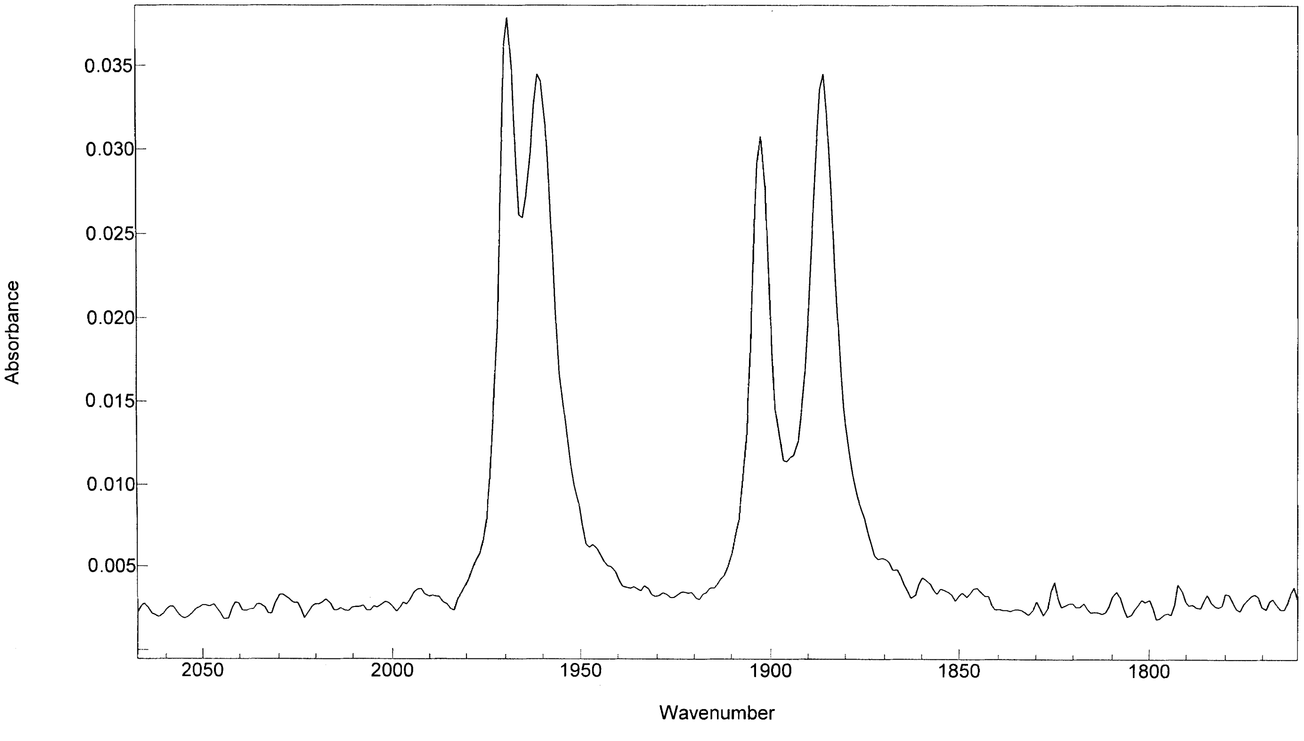

Figure 6. The IR spectrum of a pentane solution of **2** at room temperature (2 cm^{-1} resolution)

simple absorbance measurements) does indeed give a value of K close to 1.7.

In conclusion, the observation of a 1:1 intensity ratio for the bands belonging to **2**′ and **2**′′ (which will be referred to as **2B** and **2A** from now on) after vapour deposition of **2** in a solid matrix at low temperature indicates that the conformers have almost equal energies in the absence of any solvent, but differ quite significantly in energy when dissolved in a polar solvent like CD_2Cl_2. As the polarity of the supporting medium decreases, so the energy difference $\Delta E(\mathbf{2A}-\mathbf{2B})$ decreases, until with the vapour at ambient temperatures it becomes so small that the thermal populations of the two forms are almost equal.[19] These conclusions are well supported by the results of the DFT calculations (B3LYP/SDD). For the optimum geometries depicted in Figure 5, which of course represent gas phase structures, $\Delta E(\mathbf{2A}-\mathbf{2B})$ was calculated to amount to only 1.4 kJ mol^{-1}. Furthermore, the calculations indicate that **2B** is more polar (5.08 D) than **2A** (4.34 D), so that **2B** is inevitably favoured by a polar solvent environment.

In summary, there would seem to be little doubt that **2**′ and **2**′′ are the conformers **2B** and **2A**, respectively. In the light of these findings and those of Bitterwolf et al.,[17] it is very likely that Rest et al. were mistaken in their interpretation of the matrix photochemistry of the analogous tungsten system, which probably merits reinvestigation. Furthermore, we have shown: (i) that the different polarities of the *endo* and *exo* conformers cause the position of the equilibrium between them to be a sensitive function of solvation, and (ii) that the conformers can be interconverted by photoexcitation.

Experimental Section

Matrix samples were formed on a CsI window held at ca. 10 K with the aid of an Air Products CS 202 Displex unit (a two-stage, closed cycle helium refrigerator) enclosed by an evacuated shroud, or alternatively by the use of a liquid helium cryostat. The temperature of the window could be varied continuously between ca. 10 and 150 K by means of a resistive heating wire wound around the cold stage of the Displex refrigerator. Temperatures were measured with a chromel vs. iron-doped gold thermocouple or with a hydrogen vapour bulb. The matrix carrier gases used were Ar, N_2, Kr and CO (B.O.C., Research grade). Samples (held at 0 °C) were deposited continuously, typically over a period of 2 hours, the rate of deposition of the material to be isolated being regulated by its own low volatility. Photolysis experiments made use of an Oriel 500-W medium pressure mercury arc. A water filter was employed to minimise the intensity of IR radiation incident upon the matrix during photolysis. In addition, absorption or Balzer's interference filters provided the means of selecting photolysis radiation confined to a predetermined range of wavelengths.

$[CpMo(CO)_2(\eta^3\text{-}C_3H_5)]$ and $[CpMo(CO)_3(\eta^1\text{-}C_3H_5)]$ were prepared according to literature procedures.[3] IR spectra were recorded with a Bruker IFS 66 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra of solutions were recorded using a Bruker AC 200 instrument operating at 200 MHz (^{1}H).

Density Functional Theory calculations were carried out with the Gaussian/DFT series of programs.[20] The B3LYP formulation of density functional theory was used employing the basis set SDD.[20] Harmonic vibrational frequencies and infrared intensities were predicted at these levels by numerical second derivatives using analytically calculated first derivatives.

Acknowledgments

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[19] Bearing in mind the shortness of the time the molecules of **2** spend in the gas phase after vaporisation from the solid until they are frozen out in Ar, we are bound to draw the following conclusions about the solid sample. If it consisted solely of **2B**, as suggested by a single crystal X-ray analysis after recrystallisation of **2** from organic solvents, and if moreover the isomerisation barrier between **2A** and **2B** really amounted to 51.5 kJmol^{-1} as determined in benzene solution, the time the molecules would require to reach thermal equilibrium of the two forms would certainly be much longer than the time actually available to them. This means either that the isomerisation barrier almost vanishes in the gas phase or — more likely — that the solid, having been collected in the vessel by condensation of gaseous **2**, already contained both isomers in almost equal proportions. The second possibility is difficult to prove, however, since it has not been possible to resolve the distinct carbonyl bands of the two isomers in the vibrational spectra of solid samples.

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