Photoreactions of group 6 metal carbonyls with olefins

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Abstract - A scheme is presented, based on preparative and mechanistic studies, concerning the
principles which govern the course of multiple photosubstitution of group 6 metal carbonyls with
olefins: (i) after initial (η^2-olefin)M(CO)_5 formation, photodetachment of CO in cis-position to the
olefin is strongly favoured over trans-CO dissociation; (ii) a (η^2-C=C)M subunit with
trans-orthogonal position of the olefins is distinctly more stable than other geometries. This is ra-
tionalized in terms of competitive demand of CO and olefin ligands for metal d electron density,
whereby the single-faced n-acceptor character of the olefin plays a crucial role.

Sequential photosubstitution of M(CO)_6 with olefins yields (η^2-olefin)M(CO)_5 and, ultimately,
trans-(η*-olefin)M(CO)_4 complexes, as verified for all three group 6 metals. Quantum yield measurements
(0.72 for W and 0.61 for Cr in the first step; ca. 0.5 for W and ca. 0.04 for Cr in the second
step; at λ = 302 nm) and studies revealing the role of cis-(η^2-olefin)_2M(CO)_4 were performed
with E-cyclooctene, which exhibits exceptionally strong bonding to transition metals. In accord
with the above principles, photosubstitution of (η^4-norbornadiene)M(CO)_4 complexes yields
(labile) fac-(η^2-olefin)(η^4-norbornadiene)M(CO)_4 and, ultimately, (stable) mer-(η^2-olefin)(η^4-nor-
bornadiene)M(CO)_4 complexes. Implications of these findings with respect to photocatalytic processes are
briefly discussed.

INTRODUCTION

Photosubstitution of group 6 metal carbonyls is a highly efficient process which provides convenient access to a large
variety of mono- and multisubstituted derivatives. Since the pioneering work by Strohmeier et al., some
25 years ago a vast amount of information has been accumulated with respect to both synthetic applications and mechanistic aspects.
Ligand effects on electronic spectra, excited state properties, and wavelength dependent phenomena with regard to quantum
yields and stereoselectivity have been thoroughly investigated. However, most of this work was concerned with systems
containing n-donor type ligands.

By contrast, reactions involving olefin complexes are far less well-documented, despite of their potential relevance to
photocatalytic processes such as isomerization, hydrogenation, and hydroisolation of mono- and diolefins. Based on
an early report, it seemed accepted that group 6 metal carbonyl complexes with η^1-coordinated mono- or diolefins are, at
best, moderately stable, which severely hampers any detailed examination of their spectroscopic and photochemical proper-
ties. Thus, for a long time, the characterization of such compounds, and the elucidation of their structures, almost
exclusively relied on infrared spectroscopic data, particularly on the CO stretching vibrational patterns. We took this dearth
as a challenge and, a few years ago, initiated a project aimed at the photochemical synthesis and isolation of η^2-olefin
complexes derived from the parent group 6 metal hexacarbonyls or from (η^4-diene)M(CO)_4 compounds. Particular
emphasis was given to stereochemical implications of primary photoreactions and possible secondary processes, to quantum
yields, and to structural features and metal-olefin bond aspects. In the following we present an up-to-date overview of our
findings, including some material previously communicated.

SEQUENTIAL PHOTOSUBSTITUTION OF M(CO)_6 WITH OLEFINS

(η^2-Olefin)M(CO)_5 and (η^2-Olefin)_2M(CO)_4 complexes

In our first approach, initially aimed at the transition metal mediated olefin coupling, we investigated the photoreactions of
hexacarbonylmolybdenum and -tungsten with α,β-unsaturated esters, expecting that electron withdrawing substituents
should stabilize the metal olefin bond. We observed, in fact, sequential photosubstitution of two CO ligands with formation of
(η^2-olefin)M(CO)_4 (1) and, ultimately, trans-(η^2-olefin)_2M(CO)_4 (2) complexes.

Extending our studies we found that other, simple olefins such as ethene, propene or cycloalkenes, can equally well be

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TABLE 1. \((\eta^2\text{-olefin})\text{M(CO)}_5\) and trans- and cis-\((\eta^2\text{-olefin})_2\text{M(CO)}_4\) complexes of group 6 metals

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>W</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acrylate</td>
<td></td>
<td></td>
<td>W</td>
<td>Mo</td>
<td></td>
</tr>
<tr>
<td>dimethyl fumarate</td>
<td></td>
<td></td>
<td>W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-cyclooctene</td>
<td>Cr</td>
<td>Mo</td>
<td>W</td>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td>Z-cyclooctene</td>
<td>Cr</td>
<td>Mo</td>
<td>W</td>
<td>(Cr)</td>
<td>Mo</td>
</tr>
<tr>
<td>propene</td>
<td>(Cr)</td>
<td>(Mo)</td>
<td>W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethene</td>
<td>(Cr)</td>
<td>(Mo)</td>
<td>(W)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\eta^2)butadiene</td>
<td>(Mo)</td>
<td>(W)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) element symbols in parantheses refer to those compounds, which were not isolated, but characterized by infrared spectroscopy.

Employed as entering ligands - and not only with molybdenum and tungsten, but also with chromium. In Table I we have listed the various mono- and disubstituted metal carbonyl complexes isolated and investigated so far. The most recent additions to this list have been the cis-isomers \((3)\) of the disubstituted derivatives. With respect to the type of complex and to the metals employed we noted the following trends in stability:

\(2 > 1 \gg 3\), and \(Cr \ll Mo < W\).

Initially we were rather surprised by the extraordinary stability of the trans-\((\eta^2\text{-olefin})\text{W(CO)}_4\) complexes, which in variable temperature NMR experiments survived even 100 °C. However, in all substances of this type high stability was a recurrent feature. Thus, for example, trans-\((\eta^2\text{-ethene})\text{Cr(CO)}_4\), previously reported to be labile in low-temperature xenon solution, proved to be stable at ambient and higher temperatures not only in the solid state, but also in solution and in the gas phase, if rigorously purified and freed from labile by-products.

An olefin deserving special attention is E-cyclooctene, which exhibits exceptionally strong bonding to transition metals in types of complexes usually known as labile. With this particular olefin sequential photosubstitution of \(\text{M(CO)}_6\) takes place with all three metals. Not only the trans-\((\eta^2\text{-olefin})\text{M(CO)}_4\), but also the \((\eta^2\text{-olefin})\text{M(CO)}_5\) complexes are stable in these cases. Figure 1 displays the course of the reaction for chromium and tungsten, which upon extended irradiation can be brought close to completion. Isolated yields of the ultimate products \(2\) range above 60 %. With these systems mechanistic studies, including quantum yield determinations, matrix isolation photochemistry, and flash photolysis experiments with time-resolved IR detection were undertaken. As a result of these investigations, and based on the following observations and arguments, we have established Scheme 1, which represents the present state of our knowledge of the particular steps and intermediates involved in the conversion of \(\text{M(CO)}_6\) into trans-\((\eta^2\text{-olefin})\text{M(CO)}_4\).

**Scheme 1**

The role of cis-\((\eta^2\text{-olefin})_2\text{M(CO)}_4\)

Obviously photolytic CO detachment from the parent hexacarbonyl is the primary photoprocess, yielding (solvated) \(\text{M(CO)}_5\), which subsequently coordinates the olefin. The kinetics of this process have been monitored by flash photolysis in combination with time-resolved infrared spectroscopy using E-cyclooctene as the olefin.
Photoreactions of group 6 metal carbonyls with olefins

1. Sequential photosubstitution of M(CO)6 with excess E-cyclooctene in n-hexane at 20 °C, λ = 302 nm. Note that the time scale is replaced by Q atm -1 and both axes are divided by the initial M(CO)6 concentration: c0 is in the order of 5 × 10^-3 mol l^-1.

Fig. 1. Sequential photosubstitution of M(CO)6 with excess E-cyclooctene in n-hexane at 20 °C, λ = 302 nm. Note that the time scale is replaced by Q atm -1 and both axes are divided by the initial M(CO)6 concentration: c0 is in the order of 5 × 10^-3 mol l^-1.

2. The next step towards the final product requires photodetachment of CO from (η^2-E-cyclooctene)W(CO)5. The electronic absorption spectrum of which is displayed in Fig. 2. Compared with W(CO)6, the complex shows the expected bathochromic shift of the absorption features in the ligand field transition region. As indicated in the attached d-orbital splitting diagram both the triple-degeneracy of the d_z^2 set and the double-degeneracy of the d_y^z set in M(CO)6 are lifted upon replacement of one CO ligand by the olefin, which is a single-faced π-acceptor ligand; thus at least one of the d_orbitals, not interacting with the olefin, is distinctly destabilized. The ordering of the two d_orbitals should affect the reactivity of the lowest metal-centered (ligand field) excited state, but is more difficult to predict on qualitative grounds. Assuming the difference to be not too large, one would expect photolabilization of both the defin and a co ligand upon ligand field excitation of the complex. The problem, whether a CO group cis or trans to the defin would be photolabilized has been addressed recently, and the cis-vacant (η^2-olefin)M(CO)4 species was predicted to be more stable. Thus one might intuitively expect a cis-bis(olefin) complex to be generated upon photosubstitution of (η^2-E-cyclooctene)W(CO)5, by contrast with the observed stable trans-product.

Identification of the actual primary photoproducts of (η^2-E-cyclooctene)W(CO)5 was attempted by low-temperature matrix isolation techniques. After 334 nm irradiation of this complex in an argon matrix at 10-12 K two products can clearly be identified on the basis of their CO stretching vibrational patterns: W(CO)6 and trans-(η^2-E-cyclooctene)W(CO)4. The cis-structure of the latter is easily distinguishable from the possible trans-structure (which would exhibit only one CO band); three bands are clearly separated, a fourth band is overlapping with W(CO)6. With respect to the relative importance of CO vs. olefin detachment the intensity pattern reveals both processes to be of the same order, CO detach-
ment eventually to be of slight predominance. This is in contrast with a recent study in alkane glasses, where olefin detachment from \((\eta^2\text{-alkene})\text{W(CO)}_5\) complexes distinctly predominated.\(^{29}\)

Having established primary photodissociation of a cis-CO group, we searched for synthetic access to cis-(\(\eta^2\text{-olefin})\text{M(CO)}_4\)) type compounds. This was achieved by the reaction of \(E\)-cyclooctene with labile \((\eta^2\text{-diene})\text{M(CO)}_4\) complexes of molybdenum and tungsten, possessing two cis-positions available for easy substitution. The cis-(\(\eta^2\text{-E-cyclooctene})\text{M(CO)}_4\) compounds (3) are merely moderately stable and have to be handled with care at ambient temperature, which hampers quantitative studies. Nevertheless, it was unambiguously proven, that thermal rearrangement to the respective trans-isomers (2) does not take place. By contrast, photoisomerization is a highly efficient process with quantum yields apparently near unity, Scheme 2, although accurate measurements are difficult. Knowing the \(E\) stretching vibrational pattern of the tungsten complex (3) we, retrospectively, were able to correlate weak features in the infrared spectra of the reaction displayed in Fig. 1 with the presence of minor quantities of that compound. Thus it is established, that the formation of (2) from (1) involves two photochemical steps: first the photosubstitution of a cis-CO group and, subsequently, cis \(\rightarrow\) trans photoisomerization of the resulting bis-olefin complex.

**Scheme 2**

![Scheme 2](image)

**Quantum yields**

In the quantum yield determinations it was not possible to separate the above mentioned two steps and, consequently, the over-all-reactions displayed in Fig. 1 were treated as only two consecutive photoprocesses, with quantum yield \(\Phi_1\) for the disappearance of \(\text{M(CO)}_6\) and \(\Phi_2\) for the disappearance of \((\eta^2\text{-E-cyclooctene})\text{M(CO)}_4\). In the case of chromium the very late appearance of the final product indicates that \(\Phi_2\) must be distinctly smaller than \(\Phi_1\). This allows neglect of the internal light filtering by the final product, and thus \(\Phi_2\) can be calculated considering only the light filter effect of \(\Phi_1\), which retrospectively is justified by the constancy of the data (given in Figure 1) up to 50 \% conversion. The average value of \(\Phi_1 = 0.61\) (Table 2) is in close agreement with that previously obtained for the analogous photosubstitution with pyridine, in accordance with the generally accepted idea that the efficiency of such photosubstitutions should be independent of the nature of the incoming ligand. The quantum yield \(\Phi_2\) was separately determined, starting with \((\eta^2\text{-E-cyclooctene})\text{Cr(CO)}_4\). As has been estimated from Fig. 1, \(\Phi_2\) is indeed smaller than \(\Phi_1\) by more than one order of magnitude (Table 2). Careful examination reveals, that \(\Phi_2\) decreases steadily as the conversion of \((\eta^2\text{-E-cyclooctene})\text{Cr(CO)}_4\) proceeds, ranging from 0.03 at ca. 5 \% conversion to 0.01 at ca. 15 \% conversion. We suspect this to be due to the back-reaction of the intermediately formed cis-(\(\eta^2\text{-E-cyclooctene})\text{Cr(CO)}_4\) with liberated carbon monoxide rather than to an unfavourable ratio of \(E\) vs. olefin photodetachment from the olefin metal pentacarbonyl. And indeed, comparing preparative runs with continuous bubbling of neat argon with runs under CO-doped argon, we observe the latter to be retarded by several orders of magnitude.

**TABLE 2.** Quantum yields \(\Phi_1\) for the disappearance of \(\text{M(CO)}_6\) and \(\Phi_2\) for the disappearance of \((\eta^2\text{-E-cyclooctene})\text{M(CO)}_4\) upon irradiation with excess \(E\)-cyclooctene, at \(\lambda = 302\) nm in \(n\)-hexane

<table>
<thead>
<tr>
<th></th>
<th>(\Phi_1)</th>
<th>(\Phi_2)</th>
</tr>
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<tbody>
<tr>
<td>(\text{M = Cr})</td>
<td>0.61 (0.67 for (\text{L = pyridine}^{22}))</td>
<td>ca. 0.04</td>
</tr>
<tr>
<td>(\text{M = W})</td>
<td>0.72 (0.75 for (\text{L = pyridine}^{22}))</td>
<td>ca. 0.5</td>
</tr>
</tbody>
</table>

Furthermore, this concept nicely explains why (i) flash photolysis of \((\eta^2\text{-ethene})\text{Cr(CO)}_4\) in the presence of ethene in the gas phase\(^{23}\) exclusively yields (short-lived) cis-(\(\eta^2\text{-ethene})\text{Cr(CO)}_4\) with no trace of the trans-isomer, (ii) in low-temperature liquid xenon solution\(^{19}\) both of the two isomers are formed, and (iii) in alkane solution at ambient temperature, no trans-(\(\eta^2\text{-ethene})\text{Cr(CO)}_4\) is formed, whereas at \(-50^\circ\text{C}\) appreciable yields are obtained.\(^{10}\) Obviously cis-(\(\eta^2\text{-ethene})\text{Cr(CO)}_4\) is substantially more labile than the analogous \(E\)-cyclooctene complex and, therefore, cooling is required to accumulate this intermediate up to a stationary concentration sufficient for light absorption to bring about the subsequent cis \(\rightarrow\) trans photoisomerization (3 \(\rightarrow\) 2 in Scheme 1). In the case of tungsten the intermediate product of type (3) should be substantially more stable. Therefore cooling is not necessary in the synthesis of trans-(\(\eta^2\text{-ethene})\text{W(CO)}_4\).\(^{10}\)

Accordingly, inspection of Fig. 1 shows that trans-(\(\eta^2\text{-olefin})\text{W(CO)}_4\) (2) formation occurs from the very beginning, indicative of a substantially larger quantum yield \(\Phi_2\). The measured data are indeed in the range of 0.5 with respect to the disappearance of the olefin metal pentacarbonyl (1). Due to the accumulation of some cis-complex 3, necessary for the
The above reasoning should also hold for other single-faced \( \pi \)-acceptor ligand combinations, such as complex.2\( \pi \) we assume that orientation of the carbene \( \pi \)-acceptor orbital perpendicular to the carbene plane, the latter was found by X-ray diffraction structure analysis to be coplanar with the olefin C=C axis.12) With these corrections the quantum yields \( \phi \), are noticeably constant (cf. Fig. 1) up to very high conversions of \( W(CO)_6 \) with an average value of 0.72. Measurements at 302 nm and 358 nm gave nearly identical results, again in good agreement with previous data obtained for the analogous reaction with pyridine.22) The quantum deficit cannot be attributed to the, albeit possible, capture of \( W(CO)_6 \) with CO, as the measurements were performed under argon with only the liberated CO present. Under such conditions, \( [CO] \ll [olefin] \), reaction of \( W(CO)_6 \) with the olefin is by far predominant, as can be seen from the rate constants obtained from flash photolysis experiments.\( L-W(CO)_5 \) complexes have been classified according to their CO vs. unique ligand photodissociation.23) With respect to this classification the \( (\pi^2-E-cyclooctene)M(CO)_5 \) complex of tungsten resembles the \('class 2 cis'\) complexes of various phosphorous ligands undergoing photosubstitution of CO and L with nearly equal quantum yield on the order of 0.3. The analogous chromium complex, at first sight, could be considered as a \('class 1'\) compound, which undergoes very inefficient CO photostabilized CO readily loose the unique ligand. However, from the above reasoning it is obvious that this would be seriously misleading. In essence the photochemistry of the chromium \( (\pi^2-E-cyclooctene)M(CO)_5 \) complex parallels that of its tungsten analogue, the apparent difference originating from the low thermal stability of the type 3 intermediate. We take this as a warning to be careful when discussing excited state properties and primary photoactivities on the basis of overall quantum yields without intimate knowledge of the mechanistic details.

**Bonding aspects**

The distinct difference in the thermodynamic stabilities of type 1 and 3 vs type 2 complexes can be rationalized on the basis of the structure of the latter, assuming that metal(d\( n \))-\( \pi \)-olefin(\( \pi^* \)) back donation makes an essential contribution to the metal-olefin bond strength. The structures of six representatives of 2 have been solved by X-ray diffraction analysis.9,26) In all cases not only the trans-orientation of the two olefins was verified, but in addition it was shown that the olefins take up an orientation with their C=C axes perpendicular to each other. Owing to their single-faced \( \pi \)-acceptor character, the two olefins in such a trans-orthogonal situation will not compete for metal(d\( n \)) electron density, thus achieving metal(d\( n \))-\( \pi \)-olefin(\( \pi^* \)) back donation (Fig. 3) more effective than could be expected in a coplanar (eclipsed) orientation.27) Moreover, structure 2 provides for minimized competition between the CO groups and the olefin units. A CO ligand (with its two orthogonal \( \pi \)-acceptor orbitals) situated trans to an olefin will strongly rive for \( \pi \) back donation, thus weakening the metal-olefin bond. This happens in both the \((\pi^2-olefin)M(CO)_5(1)\) and the \( cis-(\pi^2-olefin)_2M(CO)_4(3)\) complexes, but is avoided in the stable \( trans-(\pi^2-olefin)_2M(CO)_4 \) compounds.

![Fig. 3. Trans-orthogonal orientation of two single-faced \( \pi \)-acceptor ligands.](image)

The above reasoning should also hold for other single-faced \( \pi \)-acceptor ligand combinations, such as mixed olefin/carbene complexes (Fig. 3), unless the linkage of two such units in a chelate ligand commands a cis-geometry. In fact, irradiation of \((diphenylcarbene)W(CO)_5\) and \(E\)-cyclooctene at \(-60^\circ C\) yields \(trans-(diphenylcarbene)(\pi^2-E\)-cyclooctene)\(W(CO)_5\). By analogy with Scheme 1, and in accordance with the observation of photochemical metathesis of a tungsten-carbene complex,26) we assume that \( cis-(diphenylcarbene)(\pi^2-E\)-cyclooctene)\(W(CO)_5\) is involved as a thermally labile intermediate, requiring cooling for stabilization in order to make subsequent cis-trans photoisomerization feasible. As expected from the orientation of the carbene \( \pi \)-acceptor orbital perpendicular to the carbene plane, the latter was found by X-ray diffraction structure analysis to be coplanar with the olefin C=C axis.12) A more recent example, which parallels our findings, is represented by the photoreaction of a chelate \( cis-(carbene-olefin)W(CO)_4\) complex with ethene. The reaction results in replacement of the olefin unit of the chelate ligand by ethene, and in the ultimate product the entering olefin is found to be \( trans\)-coplanar with the carbene unit.29)
Preparative applications of ($\eta^2$-Z-cyclooctene)M(CO)$_5$ complexes

For preparative purposes, advantage can be taken of the low stability of the olefin metal pentacarbonyls. The preparation of photosensitive L-M(CO)$_5$ complexes is commonly performed by "indirect" photosubstitution via the generation of the labile THF-M(CO)$_5$ derivatives, which subsequently to the irradiation period undergo exchange for a stronger binding ligand in the dark. The use of, e.g., ($\eta^2$-Z-cyclooctene)M(CO)$_5$ represents a convenient alternative to this traditional procedure. The Z-cyclooctene complexes have the particular advantage of being readily accessible as pure, crystalline materials, free from both residual M(CO)$_5$ and auxiliary ligand.

An intriguing example, among others, is the reaction of ($\eta^2$-Z-cyclooctene)Cr(CO)$_6$ with $^{13}$CO, which yields specifically mono-labelled Cr(CO)$_5$(CO). Employing the 'THF method', contamination with residual, unlabelled Cr(CO)$_6$ would be almost unavoidable, and direct irradiation of Cr(CO)$_6^{13}$CO definitely would result in a scrambled mixture of isotopomers with statistical distribution of the label.

PHOTOREACTIONS OF ($\eta^4$-DIENE)M(CO)$_4$ COMPLEXES

An equally thorough investigation of the photoreactions of group 6 ($\eta^4$-diene)M(CO)$_4$ complexes was appealing for two reasons. Firstly, such compounds are involved in the photocatalytic hydrogenation and hydrosilation of diene substrates with group 6 metal carbonyls, but are known not to be the active catalyst. Further irradiation is necessary to generate the active species, the identity of which is still a matter of debate. Secondly, natural scientific curiosity demands to inquire whether the extraordinary stability of the trans-($\eta^2$-C=C)M subunit would also govern the photochemical synthesis and stereochemistry of the hitherto unknown olefin substituted NBD-M(CO)$_3$ compounds.

Matrix isolation studies

Irradiation of ($\eta^2$-1,3-diene)Cr(CO)$_3$ complexes in low-temperature matrices results in detachment of both the diene and CO, as monitored by infrared spectroscopy. The latter process is by far predominant and invariably occurs at an axial position, apparently the site adjacent to the 'open' end of the 1,3-diene, yielding the unsaturated species fac-($\eta^2$-diene)Cr(CO)$_3$ (6). Likewise, 253 nm irradiation of ($\eta^4$-NBD)Cr(CO)$_4$ in solid argon at 10-12 K yields fac-($\eta^4$-NBD)Cr(CO)$_3$ (7). However, upon irradiation in the 300-380 nm region a second product, mer-($\eta^4$-NBD)Cr(CO)$_3$ (8), is formed in addition to 7. Noticeably, irradiation into the characteristic, distinctly different long-wavelength electronic absorptions of the unsaturated species results in interconversion of 7 and 8, rather than in recovery of the starting material. Interestingly, fac $\Rightarrow$ mer photoisomerization seems to proceed much more efficiently than the reverse process. We saw no evidence for formation of the cis-unsaturated ($\eta^2$-NBD)Cr(CO)$_4$ species.

Syntheses of ($\eta^2$-olefin)$($\eta^4$-norbornadiene)M(CO)$_3$ complexes

Irradiation of ($\eta^4$-norbornadiene)M(CO)$_3$ complexes in the presence of various olefins (ethene, Z-cyclooctene, and E-cyclooctene) results in the substitution of CO, yielding the respective, hitherto unknown mer-($\eta^2$-olefin)($\eta^4$-norbornadiene)M(CO)$_3$ derivatives (10). The stability increases in the order Cr < Mo < W and, once again, E-cyclooctene gave proof of its exceptional coordination ability. Using this olefin we have demonstrated the intermediacy of (thermally labile) fac-($\eta^2$-olefin)($\eta^4$-norbornadiene)M(CO)$_3$ (9) in the formation of 10. Scheme 3. Careful monitoring of the photo-reaction of ($\eta^4$-NBD)W(CO)$_5$ with E-cyclooctene revealed that up to ca. 15 % conversion of the starting material the fac-isomer of type 9 was the only product, which could thus be isolated and further investigated. At ambient temperature in the dark a slow isomerization into 10 takes place, whereas under irradiation this proved to be a very efficient process.

The initial formation of the axially substituted complex 9 is in accord with the previously reported photo-initiated

Scheme 3
One particular lesson to be drawn from our findings is that the ready formation of the extraordinarily stable of this kind towards the most stable final product. With regard to the stereoselective CO photodissociation, a correlation with carbonyl was established by X-ray diffraction structure analysis of mer-(1,4-ethene)(1,4-norbornadiene)W(CO)₅. With pleasure we note, once again, the trans-orthogonal configuration of two single-faced ligands to be the pivotal feature guiding a reaction of this kind towards the most stable final product.

CONCLUSION

One might take the above reactions of (diene)M(CO)₄ complexes as a model for the creation of a vacant site necessary iii the photocatalytic diene hydrogenation in order to coordinate an H₂ molecule. It is then interesting to note that the reported exclusive cis-1,4-hydrogenation of 1,3-dienes coincides with the observed exclusive axial position of CO photodetachment. The facile isomerization of the analogous NBD-complex fragment into the equatorially unsaturated species may thus explain why this diene yields two hydrogenation products, norbornene and nortricylene, hydrogenated in the 1,2 and a 1,4- analogous fashion. The former reaction mode has previously been discussed in terms of primary photo-decelation of the norbornadiene ligand, however, there is no concrete evidence for such a process.

One particular lesson to be drawn from our findings is that the ready formation of the extraordinarily stable trans-orthogonal (1,2-C=CH₂)₄M subunit serves as a 'black hole' in any photocatalytic activity in group 6 metal carbonyl / olefin systems, requiring continuous photochemical re-creation of the active species.

With regard to the stereoselective CO photodissociation, a correlation with ¹³C NMR data seems possible. We note that CO groups in cis-position to olefin ligands, exhibiting the less pronounced downfield shift in the ¹³C NMR spectra, are photolabile. This may be attributed to weaker metal(dₓ)→CO(n⁻) back donation, favouring detachment of cis-CO ligands. A similar correlation between CO photodetachment and CO force constants has been discussed previously. It certainly seems worthwhile to look out for further examples of such effects; if a general trend could be established it would carry valuable predictive power.

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