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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)$_2$M subunit with *trans-orthogonal* position of the olefins is distinctly more stable than other geometries. This is rationalized in terms of competitive demand of CO and olefin ligands for metal d_π electron density, whereby the single-faced π-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^2-olefin)$_2$M(CO)$_4$, 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)$_2$M(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)$_3$ and, ultimately, (stable) *mer*-(η^2-olefin)(η^4-norbornadiene)M(CO)$_3$. 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.*$^{1)}$ some 25 years ago a vast amount of information has been accumulated$^{2)}$ 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$^{3)}$ such as isomerization,$^{4)}$ hydrogenation,$^{5,6)}$ and hydrosilation$^{7)}$ of mono- and diolefins. Based on an early report$^{8)}$ it seemed accepted that group 6 metal carbonyl complexes with η^2-coordinated mono- or diolefins are, at best, moderately stable, which severely hampers any detailed examination of their spectroscopic and photochemical properties. 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.$^{9,10,11,12,13)}$

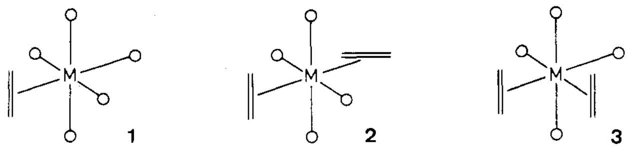
SEQUENTIAL PHOTOSUBSTITUTION OF M(CO)$_6$ WITH OLEFINS

(η^2-Olefin)M(CO)$_5$ and (η^2-olefin)$_2$M(CO)$_4$ complexes

In our first approach,$^{9)}$ 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)$_5$ (**1**) and, ultimately, *trans*-(η^2-olefin)$_2$M(CO)$_4$ (**2**) complexes.

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

TABLE 1. (η^2-Olefin)M(CO)$_5$ and *trans*- and *cis*-(η^2-Olefin)$_2$M(CO)$_4$ complexes of group 6 metals[a]



	1	2	3
methyl acrylate	W	Mo W	
dimethyl fumarate	W	W	
E-cyclooctene	Cr Mo W	Cr Mo W	Mo W
Z-cyclooctene	Cr Mo W	(Cr) Mo W	
propene	(Cr)	W	
ethene	(Cr) (Mo) (W)	Cr Mo W	
η^2-butadiene	(Mo) (W)	Mo W	

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

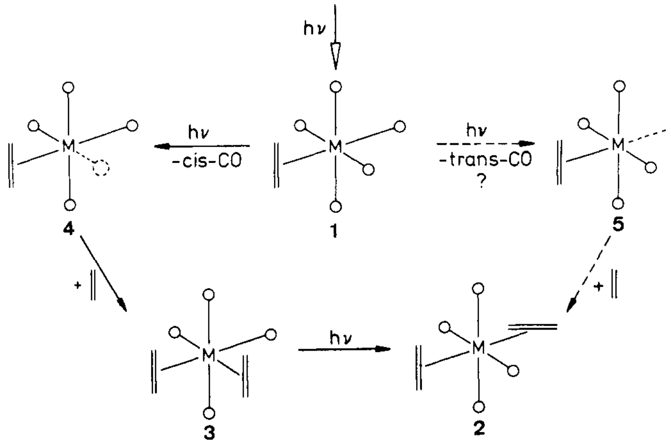
employed as entering ligands - and not only with molybdenum and tungsten, but also with chromium. In Table 1 we have listed the various mono- and disubstituted metal carbonyl complexes isolated and investigated so far. The most recent additions to this list have been the *cis*-isomers (**3**) of the disubstituted derivatives. With respect to the type of complex and to the metals employed we noted the following trends in stability:

$$2 > 1 \gg 3, \quad \text{and} \quad \mathrm{Cr} \ll \mathrm{Mo} < \mathrm{W}.$$

Initially we were rather surprised by the extraordinary stability of the *trans*-(η^2-olefin)$_2$W(CO)$_4$ complexes,9) 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*-(η^2-ethene)$_2$Cr(CO)$_4$, previously reported14) to be labile in low-temperature xenon solution, proved10) 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.15) With this particular olefin sequential photosubstitution of M(CO)$_6$ takes place with all three metals. Not only the *trans*-(η^2-olefin)$_2$M(CO)$_4$, but also the (η^2-olefin)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 detection16) 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 M(CO)$_6$ into *trans*-(η^2-olefin)$_2$M(CO)$_4$.

Scheme 1



The role of *cis*-(η^2-olefin)$_2$M(CO)$_4$

Obviously photolytic CO detachment from the parent hexacarbonyl is the primary photoprocess, yielding (solvated) 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,16) using *E*-cyclooctene as the olefin.

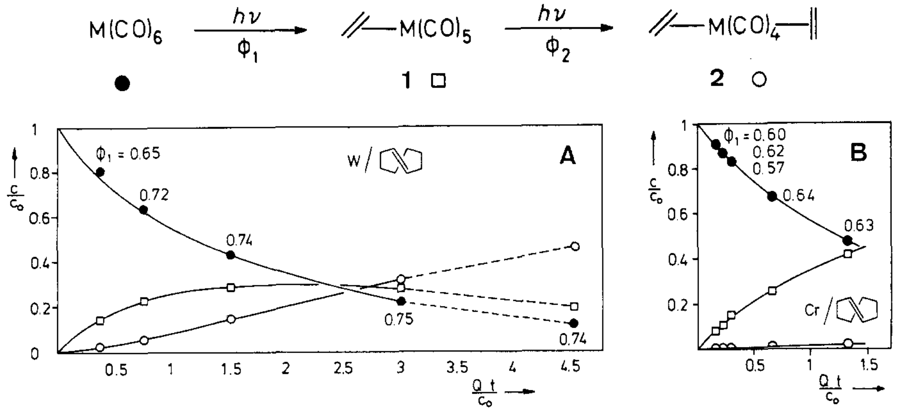


Fig. 1. Sequential photosubstitution of $M(CO)_6$ with excess *E*-cyclooctene in *n*-hexane at 20 °C, λ = 302 nm. Note that the time scale is replaced by $Q_{abs} \cdot t$ and both axes are divided by the initial $M(CO)_6$ concentration; c_o is in the order of $5 \cdot 10^{-3}$ mol l^{-1}.

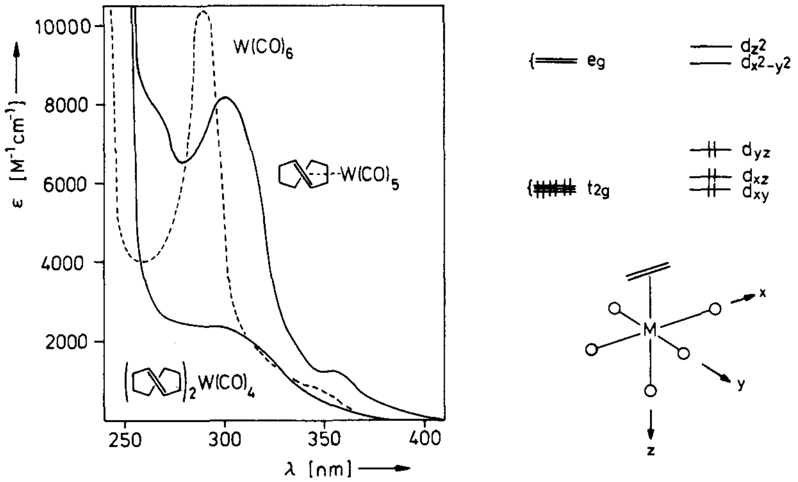


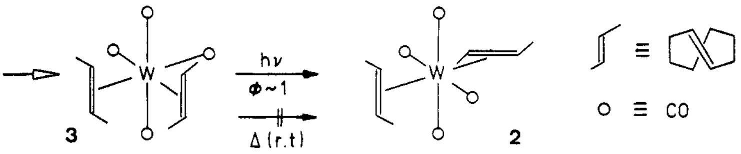
Fig. 2. Electronic absorption spectra of $W(CO)_6$, (η^2-*E*-cyclooctene)$W(CO)_5$ and *trans*-(η^2-*E*-cyclooctene)$_2W(CO)_4$ in *n*-hexane.

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 $W(CO)_6$[17] 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_π (t_{2g}) set and the double-degeneracy of the d_σ (e_g) 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_π orbitals, not interacting with the olefin, is distinctly destabilized. The ordering of the two d_σ 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 olefin and a CO ligand upon ligand field excitation of the complex. The problem, whether a CO group *cis* or *trans* to the olefin would be photolabilized has been addressed recently,[18] 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: $W(CO)_5$[19] and *cis*-vacant (η^2-*E*-cyclooctene)$W(CO)_4$ (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 $W(CO)_5$. With respect to the relative importance of CO *vs.* olefin detachment the intensity pattern reveals both processes to be of the same order, CO detachment eventually to be of slight predominance. This is in contrast with a recent study in alkane glasses, where olefin detachment from $(\eta^2\text{-alkene})W(CO)_5$ complexes distinctly predominated.[20)]

Having established primary photodissociation of a *cis*-CO group, we searched for **synthetic access to** ***cis*-$(\eta^2\text{-olefin})_2M(CO)_4$** type compounds. This was achieved by the reaction of *E*-cyclooctene with labile $(\eta^4\text{-diene})M(CO)_4$ complexes of molybdenum and tungsten, possessing two *cis*-positions available for easy substitution. The *cis*-$(\eta^2\text{-}E\text{-cyclooctene})_2M(CO)_4$ 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 CO 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* → *trans* photoisomerization of the resulting bis-olefin complex.

Scheme 2



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 ϕ_1 for the disappearance of $M(CO)_6$ and ϕ_2 for the disappearance of $(\eta^2\text{-}E\text{-cyclooctene})M(CO)_5$. In the case of chromium the very late appearance of the final product indicates that ϕ_2 must be distinctly smaller than ϕ_1. This allows neglection of the internal light filtering by the final product, and thus ϕ_1 can be calculated considering only the light filter effect of **1** ,[21)] which retrospectively is justified by the constancy of the data (given in Figure 1) up to 50 % conversion. The average value of ϕ_1 = 0.61 (Table 2) is in close agreement with that previously obtained for the analoguous 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 ϕ_2 was separately determined, starting with $(\eta^2\text{-}E\text{-cyclooctene})Cr(CO)_5$. As has been estimated from Fig. 1, ϕ_2 is indeed smaller than ϕ_1 by more than one order of magnitude (Table 2). Careful examination reveals, that ϕ_2 decreases steadily as the conversion of $(\eta^2\text{-}E\text{-cyclooctene})Cr(CO)_5$ proceeds, ranging from 0.05 at ca. 5 % conversion to 0.03 at ca. 15 % conversion. We suspect this to be due to the back-reaction of the intermediately formed *cis*-$(\eta^2\text{-}E\text{-cyclooctene})_2Cr(CO)_4$ with liberated carbon monoxide rather than to an unfavourable ratio of CO *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 ϕ_1 for the disappearance of $M(CO)_6$ and ϕ_2 for the disappearance of $(\eta^2\text{-}E\text{-cyclooctene})M(CO)_5$ upon irradiation with excess *E*-cyclooctene, at λ = 302 nm in *n*-hexane

	ϕ_1		ϕ_2
M = Cr	0.61	(0.67 for L = pyridine[22)])	ca. 0.04
M = W	0.72	(0.75 for L = pyridine[22)])	ca. 0.5

Furthermore, this concept nicely explains why (i) flash photolysis of $(\eta^2\text{-ethene})Cr(CO)_5$ in the presence of ethene in the gas phase[23)] exclusively yields (short-lived) *cis*-$(\eta^2\text{-ethene})_2Cr(CO)_4$ with no trace of the *trans*-isomer, (ii) in low-temperature liquid xenon solution[14)] both of the two isomers are formed, and (iii) in alkane solution at ambient temperature no *trans*-$(\eta^2\text{-ethene})_2Cr(CO)_4$ is formed, whereas at -50 °C appreciable yields are obtained.[10)] Obviously *cis*-$(\eta^2\text{-ethene})_2Cr(CO)_4$ 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* → *trans* photoisomerization (**3** → **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*-$(\eta^2\text{-ethene})_2W(CO)_4$.[10)]

Accordingly, inspection of Fig. 1 shows that *trans*-$(\eta^2\text{-olefin})_2W(CO)_4$ (**2**) formation occurs from the very beginning, indicative of a substantially larger quantum yield ϕ_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 subsequent photoisomerization into **2** , data for the appearance of the final type **2** product are smaller. Trivially they cannot exceed 0.5 as they represent the overall result of two consecutive photochemical steps.

With respect to the quantum yields ϕ_1, representing the disappearance of $W(CO)_6$, accounting for internal light filter effects of both the mono- and the disubstituted products **1** and **2** is indispensible, obvious from the electronic spectra (Fig. 2) of the compounds involved in this system. Therefore ϕ_1 was calculated by using the formalism developed for a photoreaction with two consecutive photochemical steps,[24)] whereby the quantum yield for the second step was taken to be $\phi_2 = 0.5$. With these corrections the quantum yields ϕ_1 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 $W(CO)_5$ with CO, as the measurements were performed under argon with only the liberated CO present. Under such conditions, [CO] << [olefin], reaction of $W(CO)_5$ with the olefin is by far predominant, as can be seen from the rate constants obtained from flash photolysis experiments.[16)]

L-$W(CO)_5$ complexes have been classified according to their CO *vs.* unique ligand photodissociation.[25)] With respect to this classification the (η^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 photosubstitution but readily looses the unique ligand. However, from the above reasoning it is obvious that this would be seriously misleading. In essence the photochemistry of the chromium (η^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 photoreactivities 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_π)$\rightarrow$olefin(π^*) 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*-positioning 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 π-acceptor character, the two olefins in such a *trans-orthogonal* situation will not compete for metal(d_π) electron density, thus achieving metal(d_π)$\rightarrow$olefin(π^*) 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 <u>two</u> orthogonal π-acceptor orbitals) situated *trans* to an olefin will strongly rival for π back donation, thus weakening the metal-olefin bond. This happens in both the (η^2-olefin)$M(CO)_5$ (**1**) and the *cis*-(η^2-olefin)$_2M(CO)_4$ (**3**) complexes, but is avoided in the stable *trans*-(η^2-olefin)$_2M(CO)_4$ compounds.

metal(d)—→olefin(π*)   metal(d)—→carbene(p)

Fig. 3. *Trans-orthogonal* orientation of two single-faced π-acceptor ligands.

The above reasoning should also hold for other single-faced π-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 °C yields *trans*-(diphenylcarbene)(η^2-*E*-cyclooctene)$W(CO)_4$. By analogy with *Scheme 1*, and in accordance with the observation of photochemical metathesis of a tungsten-carbene complex,[28)] we assume that *cis*-(diphenylcarbene)(η^2-*E*-cyclooctene)$W(CO)_4$ 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 π-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 $(\eta^2\text{-}Z\text{-cyclooctene})M(CO)_5$ complexes

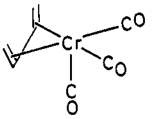
For preparative purposes, advantage can be taken of the low stability of the olefin metal pentacarbonyls. The preparation of photosensitive $L\text{-}M(CO)_5$ complexes is commonly performed by "indirect" photosubstitution via the generation of the labile $THF\text{-}M(CO)_5$ derivatives, which subsequent to the irradiation period undergo exchange for a stronger binding ligand in the dark.[1)] The use of, *e.g.*, $(\eta^2\text{-}Z\text{-cyclooctene})M(CO)_5$ 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 $M(CO)_6$ and auxiliary ligand. An intriguing example, among others,[11,30)] is the reaction of $(\eta^2\text{-}Z\text{-cyclooctene})Cr(CO)_5$ with ^{13}CO, which yields specifically mono-labelled[11)] $Cr(CO)_5(^{13}CO)$. 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 $(\eta^4\text{-DIENE})M(CO)_4$ COMPLEXES

An equally thorough investigation of the photoreactions of group 6 $(\eta^4\text{-diene})M(CO)_4$ 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*-$(\eta^2\text{-}C{=}C)_2M$ subunit would also govern the photochemical synthesis and stereochemistry of the hitherto unknown olefin substituted $NBD\text{-}M(CO)_3$ compounds.

Matrix isolation studies

Irradiation of $(\eta^4\text{-1,3-diene})Cr(CO)_4$ complexes in low-temperature matrices[13)] 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*-$(\eta^4\text{-diene})Cr(CO)_3$ (**6**). Likewise, 253 nm irradiation of $(\eta^4\text{-NBD})Cr(CO)_4$ in solid argon at 10-12 K yields *fac*-$(\eta^4\text{-NBD})Cr(CO)_3$ (**7**). However, upon irradiation in the 300-380 nm region a second product, *mer*-$(\eta^4\text{-NBD})Cr(CO)_3$ (**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* → *mer* photoisomerization seems to proceed much more efficiently than the reverse process. We saw no evidence for formation of the *cis*-unsaturated $(\eta^2\text{-NBD})Cr(CO)_4$ species.



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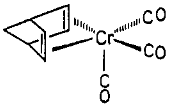

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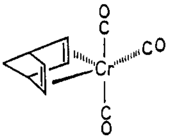

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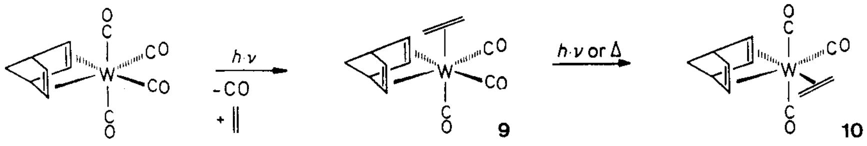
Syntheses of $(\eta^2\text{-olefin})(\eta^4\text{-norbornadiene})M(CO)_3$ complexes

Irradiation of $(\eta^4\text{-norbornadiene})M(CO)_4$ 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*-$(\eta^2\text{-olefin})(\eta^4\text{-norbornadiene})M(CO)_3$ 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*-$(\eta^2\text{-olefin})(\eta^4\text{-norbornadiene})M(CO)_3$ (**9**) in the formation of **10** , *Scheme 3*. Careful monitoring of the photoreaction of $(\eta^4\text{-NBD})W(CO)_4$ 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



incorporation of ^{13}CO into the axial position of (η^4-NBD)M(CO)$_4$.[6b)] The geometry of the stable ultimate product **10** was established by X-ray diffraction structure analysis of *mer*-(η^2-ethene)(η^4-norbornadiene)W(CO)$_3$.[31)] 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 in the photocatalytic diene hydrogenation in order to coordinate an H_2 molecule. It is then interesting to note that the reported exclusive *cis*-1,4-hydrogenation[5)] of 1,3-dienes coincides with the observed exclusive axial position of CO photodetachment. The facile isomerization of the analogous NBD-complex fragment **7** into the equatorially unsaturated species **8** may thus explain why this diene yields two hydrogenation products, norbornene and nortricyclene, hydrogenated in the 1,2 and a 1,4- analogous fashion. The former reaction mode has previously[6)] been discussed in terms of primary photo-dechelation 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* (η^2-C=C)$_2$M 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 ^{13}C NMR data seems possible. We note that CO groups in *cis*-position to olefin ligands, exhibiting the less pronounced downfield shift in the ^{13}C NMR spectra, are photolabile. This may be attributed to weaker metal(d_π)$\rightarrow$CO(π^*) back donation, favouring detachment of *cis*-CO ligands. A similar correlation between CO photodetachment and CO force constants has been discussed previously.[25)] 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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