Coordination Chemistry Reviews, 111 (1991) 325–330
Elsevier Science Publishers B.V., Amsterdam

Photochemical olefin activation by transition metal complexes

T. van Houwelingen, D.J. Stufkens and A. Oskam

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

1. INTRODUCTION

Transition metals show a large variety in their reactivity towards olefins. We have studied three of these reaction types: *a)* coordination of the olefin to a 16-electron metal centre after photochemical dissociation of a 2-electron donating ligand; *b)* coordination of the olefin to a 17-electron centre, formed by photochemical dissociation of a 1-electron donating ligand and *c)* thermal electron transfer to the olefin after reaction *a)* or *b)*.

2. COORDINATION TO A 16-ELECTRON METAL CENTRE

A well known example of a photochemical reaction in which an olefin is involved as a 2- or 4-electron donating ligand is the photochemical formation of $Cr(CO)_5(\eta^2$-diene) and $Cr(CO)_4(\eta^4$-diene) out of $Cr(CO)_6$ and a diene [1]. Upon further irradiation of $Cr(CO)_4(\eta^4$-diene) in the presence of H_2 the coordinated diene is hydrogenated [2]. Instead of new C-H bonds, C-C bonds are formed when $Cr(CO)_3(\eta^6$-cycloheptatriene), **1**, is irradiated in the presence of a conjugated diene [3], resulting in the formation of a coordinated bicyclo–undecatriene ligand in the product **2**. We have investigated the mechanism of this reaction [4]. The primary photoprocesses [3] were studied by matrix isolation photochemistry, the secondary

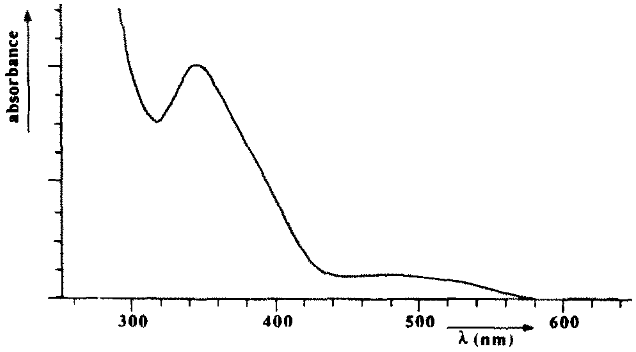
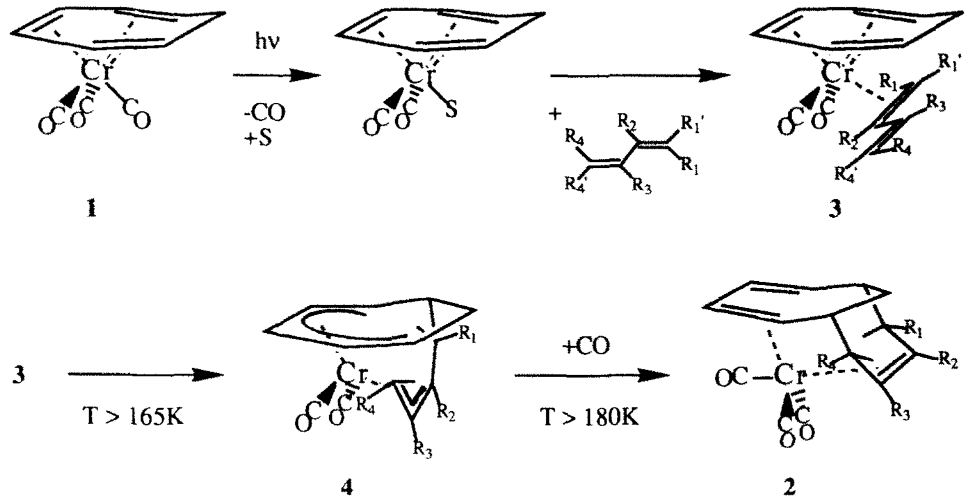


Figure 1. The UV/Vis spectrum of **1** in pentane.

0010-8545/91/$03.50 © 1991 Elsevier Science Publishers B.V. All rights reserved.



S= Solvent

Scheme 1. The mechanism of the photochemical C-C coupling reaction between **1** and conjugated dienes.

thermal reactions by low temperature solution experiments, mainly in liquid xenon, which is able -due to its inertness- to stabilize highly unstable intermediates [5].

2.1. The primary photoprocesses

The UV/Vis spectrum of complex **1** (see Figure 1) shows two bands. The reactions taking place upon irradiation into the composite 350 nm band have been studied by Hooker and Rest [6], while we have irradiated into the low intensity ligand field transition around 500 nm [4]. Irradiation with $\lambda > 280$ nm resulted in both CO loss and hapticity change of the triene ring. The latter process was only observable in the presence of excess CO. Which Cr-CO or Cr-olefin bond was broken depended, however, on the wavelength of irradiation.

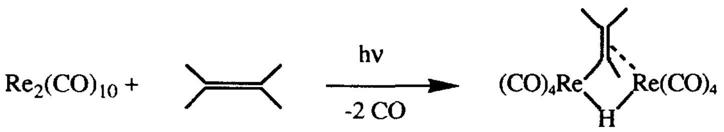
2.2. The secondary thermal reaction steps

The secondary thermal reaction steps are represented in Scheme 1. The mechanism is wavelength independent at $\lambda_{irr} > 365$ nm. Irradiation of **1** in the presence of a diene (usually pentadiene) resulted exclusively in the formation of a thermally unstable dicarbonyl complex. No trace of a tricarbonyl product was observed, which means that no hapticity change of the triene ring is involved in the C-C coupling reaction [3]. By comparing the CO-stretching frequencies and force constants of the products of a series of mono- and diolefins and P- and N-donors [7] the dicarbonyl vibrations were assigned to $Cr(CO)_2(\eta^6\text{-}C_7H_8)(\eta^2\text{-diene})$, **3**.

Upon raising the temperature of the diolefin reaction mixtures to 165 K complex **3** disappeared with concomitant formation of a second dicarbonyl complex, **4**. Contrary to those of product **3**, the CO-stretching vibrations of this product were not influenced by the presence of methyl substituents on the diene. The new dicarbonyl vibrations are assigned to a product already observed by Kreiter [3]: $Cr(CO)_2(\eta^8$-olefin), in which the olefin is the product of the formation of one C-C bond between the diene and the triene ring. Upon further raising the temperature to 180 K the final product **2** was formed, most probably via a concerted process in which the dissociated CO reacted back and the second C-C bond formation occurred.

3. COORDINATION TO A 17-ELECTRON METAL CENTRE

A 17-electron metal centre which is highly reactive towards olefins is the rheniumpentacarbonyl radical, which reacts for instance with monoolefins [8], Reaction 1, and with cumulated diolefins (allenes) [9]. In several steps of the allene reaction CO dissociation is involved. However, since the products absorb in the same wavelength region as the starting materials, it is impossible to determine whether a secondary process is thermal or photochemical.



(1)

We have therefore decided to generate the rheniumpentacarbonyl radicals with visible light. This was achieved by using $(CO)_5ReRe(CO)_3(\alpha$-diimine) complexes, **5**, as the starting material. In these complexes a $Re(CO)_3(\alpha$-diimine) fragment (α-diimine= phenantroline or 1,4-p-tolyl-1,4-diazabutadiene) serves as a chromophoric group. Irradiation into the long wavelength transition, see Figure 2, results exclusively in metal-metal bond homolysis, producing rheniumpentacarbonyl and rheniumtricarbonyl-α-diimine radicals [10]. The allene used was phenylallene.

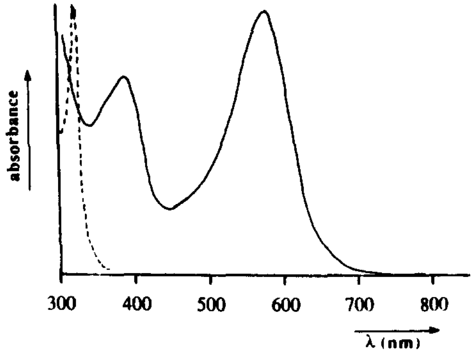
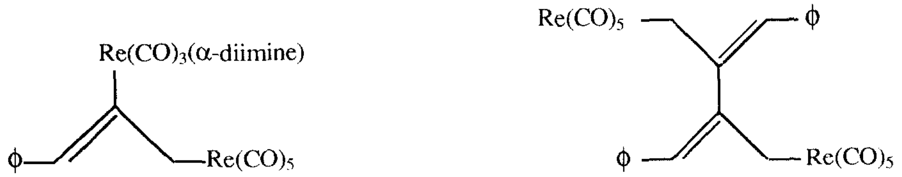


Figure 2. The UV/Vis spectra of **5** (—) and $Re_2(CO)_{10}$ (- - -).

The preliminary results turned out to be dependent on the temperature of the reaction mixture. Irradiation at 240 K in toluene resulted in the formation of two rheniumpentacarbonyl products, having their highest CO stretching frequencies at 2143 and 2132 cm^{-1} respectively. After raising the temperature one of these pentacarbonyl bands remained (at 2133 cm^{-1}), while a tetracarbonyl CO-band showed up at 2063 cm^{-1}. The proposed reaction, (2) [9], involves an attack of two rheniumpentacarbonyl radicals at one allene molecule, followed by CO loss and η^3-coordination of the allenic unit to the resulting rheniumtetracarbonyl fragment upon raising the temperature.

(2)

At still lower temperatures an unstable tricarbonyl product with low tricarbonyl frequencies (2010, 1890 and 1875 cm^{-1}) was formed, while a pentacarbonyl band showed up at 2118 cm^{-1}. The product is assigned to $(CO)_5$Re-phenylallene-Re$(CO)_3$(α-diimine), **6**, see Chart 2. The tricarbonyl frequencies are typical for a zerovalent Re$(CO)_3$(α-diimine) species, σ-coordinated to a 1-electron donating ligand [11], while the pentacarbonyl band most probably belongs to a Re$(CO)_5$ coordinated to an olefin, compare for instance complex **7** (Chart 1) [9].



6 **7**

Chart 1

4. ELECTRON TRANSFER REACTIONS

The electrophilic olefin tetracyanoethylene (TCNE) reacts with a variety of organometallic complexes [12]. Examples are insertion in the tin-tin bond in Sn_2Me_6 [13] and THF substitution in Cp*Mn$^{I}(CO)_2$(THF), followed by electron transfer from the metal to the olefin [14]. We have studied the reaction between $Ph_3SnM(CO)_3$(α-diimine) (M= Mn, Re; α-diimine= bpy', 4,4'-dimethyl-2,2'-bipyridine, and R-DAB, 1,4-di-R-1,4-diazabutadiene, with R=i-propyl, t-butyl) and TCNE. The manganese complexes show only CO dissociation upon irradiation, enabling us to study the reaction between TCNE and a 16-electron metal-α-diimine system [15]. The rhenium complexes, on the other hand, show only metal-metal bond homolysis and can therefore be used to study the interaction between TCNE and a metal-α-diimine radical [12a,12b,15]. TCNE was chosen because of its high reactivity and because of its two different coordination modes, via a nitrogen or via the ethylenic unit, which are clearly distinguishable by their specific influence on the CN-stretching vibrations [14].

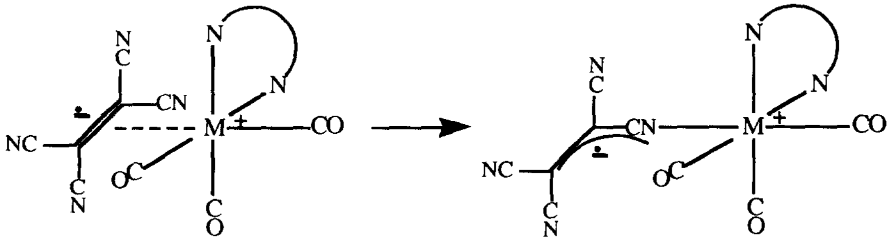
4.1. The photochemical reactivity of the complexes

At lower temperatures (below 213 K) the manganese complexes showed the expected CO substitution reaction with TCNE. The TCNE coordinates via a nitrogen atom. The CO-stretching frequencies were very high for a dicarbonyl complex but a similar behaviour has e.g. been observed for $Cp^*Mn(CO)_2(TCNE)$ [14]. Upon substituting the THF ligand in $Cp^*Mn(CO)_2(THF)$ by TCNE the CO-stretching vibrations shift from 1910 and 1836 cm^{-1} [16] to 1985 and 1950 cm^{-1} respectively. In $Ph_3SnMn(CO)_2$(t-butyl-DAB)L the frequencies shift from 1884 and 1810 cm^{-1} (L= THF, [15]) to 1951 and 1880 cm^{-1} respectively (L= TCNE).

The high CO-stretching frequencies indicate an almost complete electron transfer from the metal to the olefin. This was confirmed by the UV/Vis spectrum, which showed the vibrational fine structure of $TCNE^{\dot{-}}$ [17]. The electronic absorption spectrum also showed an intense band at λ= 900 nm or higher (900 nm is the apparatus maximum). The nature of this band could not be determined, but it most likely belongs to a charge transfer transition between the metal and the TCNE ligand. The product is thermally unstable. Upon raising the temperature a back reaction occurs to give the starting material. The rhenium complexes showed metal-metal bond homolysis upon irradiation, followed by coordination of the TCNE. Again an electron transfer to the olefin was observed, resulting in the formation of $Re^I(CO)_3(\alpha\text{-diimine})(TCNE^{\dot{-}})$, **8**.

4.2. Thermal reactions

Product **8** of the photochemical reaction of the rhenium complexes was thermally unstable. It isomerized to another tricarbonyl complex, **9**. Surprisingly product **8** could also be obtained thermally, in a slow reaction. The manganese complexes formed similar thermal reaction products, **10** and **11**, but the reactions were much faster. We have characterized the products of the thermal reaction of $Ph_3SnMn(CO)_3(bpy')$. The most characteristic CN-stretching frequencies (2225 and 2195 cm^{-1} in **10** and 2210 and 2130 cm^{-1} in **11** respectively) indicate a π-coordination of the TCNE ligand in **8** and **10** and a σ-coordination in **9** and **11**, see Reaction 3 [14].



(3)

8 (M= Re), **10** (M= Mn) **9** (M= Re), **11** (M= Mn)

5. ACKNOWLEDGEMENT

The assistance of the following persons is gratefully acknowledged. R.H. Hooker and A. Rest provided results prior to publication. W.G.J. de Lange synthesized the α-diimine complexes. B.R. Rossenaar performed a large part of the TCNE experiments. H. Luyten, G.C. Schoemaker and T.L. Snoeck offered technical assistance. The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Research (NWO) are thanked for financial support.

6. REFERENCES

1. a) I. Fischler, M. Budzwait and E.A. Koerner von Gustorf, J. Organomet. Chem., 105 (1976) 325.
   b) S. Özkar, Ph. D. thesis, T.U. München, 1976.
2. J. Nasielski, P. Kirsch and L. Wilputte-Steinert, J. Organomet. Chem., 27 (1971) C13. See also: S.A. Jackson, P.M. Hodges, M. Poliakoff, J.J. Turner and F.-W. Grevels, J. Am. Chem. Soc., 112 (1990) 1221.
3. C.G. Kreiter, Adv. Organomet. Chem., 26 (1986) 297.
4. T. van Houwelingen, D.J. Stufkens and A. Oskam, Organomet., submitted for publication.
5. D. Jones, New Scientist Dec. 16 (1984).
6. R.H. Hooker and A.J. Rest, personal communication.
7. a) W.P. Anderson, W.G. Blenderman, K.A. Drews, J. Organometal. Chem., 42 (1972) 139.
   b) M. Djazayeri, C.G. Kreiter, H.M. Kurz, M. Lang, S. Özkar, Z. Naturforsch., 31b (1976) 1238.
8. P.O. Nubel and T.L. Brown, J. Am. Chem. Soc., 104 (1982) 4955.
9. a) W. Michels, W., Ph. D. thesis, University of Kaiserslautern, (1988).
   b) C.G. Kreiter, W. Michels and R. Exner, Z. Naturforsch., 45b (1990) 793.
10. D.L. Morse and M.S. Wrighton, J. Am. Chem. Soc., 98 (1976) 3931.
11. a) J.C. Luong, R.A. Faltyrek, M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 1597.
    b) J.C. Luong, R.A. Faltyrek, M.S. Wrighton, J. Am. Chem. Soc., 102 (1980) 7892.
    c) R.R. Andréa, W.G.J. de Lange, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 149 (1988) 77.
12. A.J. Fatiadi, Synthesis, (1987) 959 and references therein.
13. O.A. Reutov, V.I. Rozenberg, G.V. Gavrilova and V.A. Nikanorov, J. Organometal. Chem., 177 (1979) 101.
14. B. Olbrich-Deußner, Renate Groß and Wolfgang Kaim, J. Organometal. Chem., 366 (1989) 155.
15. R.R. Andréa, W.G.J. de Lange, D.J. Stufkens and A. Oskam, Inorg. Chem., 28 (1989) 318.
16. a) E.O. Fischer and M. Herberhold, Experientia Supplementum, IX (1964) 259.
    b) W.A. Herrmann, R. Serrano and J. Weichmann, J. Organometal. Chem., 246 (1983) C57.
17. O.W. Webster, W. Mahler and R.F. Benson, J. Am. Chem. Soc., 84 (1962) 3678.