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PRIMARY PHOTOCHEMICAL PROCESS IN NORBORNADIENECHROMIUM TETRACARBONYL

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Summary

Low-temperature photolysis of $NbdCr(CO)_4$(I) (Nbd = norbornadiene) in the presence of triphenylphosphine yields *trans*-$NbdCr(CO)_3[P(C_6H_5)_3]$. The quantum yields of the room-temperature photoinduced conversion of I in the presence of H_2, of $P(C_6H_5)_3$ and of both reagents, are respectively 0.140, 0.105 and 0.104. Primary photoinduced formation of monodentate I is shown to account for these observations.

The high photostability of norbornadienechromium tetracarbonyl ($NbdCr(CO)_4$) (I) in deaerated aliphatic solvents, led us to the conclusion that the main primary photochemical process consists in conversion of the bidentate norbornadiene—chromium bond into a two-electron bond [1]. We thus assumed that monodentate norbornadienechromium tetracarbonyl was the active species in the photoinduced hydrogenation of norbornadiene in the presence of I.

Later Darensbourg and Nelson [2] showed that both the carbonyl ligands *cis* to norbornadiene were easily and preferentially substituted by ^{13}CO under irradiation, and proposed square-pyramidal $NBdCr(CO)_3$ with *cis*-vacancy, as the first photoinduced intermediate. We observed that room-temperature irradiation of I in the presence of $P(C_6H_5)_3$ yielded *trans*-$NbdCr(CO)_3[P(C_6H_5)_3]$ (II) [3].

Wrighton and Schroeder [4] reported the catalytic action of $Cr(CO)_3(CH_3CN)_3$ in the 1,4-addition of H_2 to 1,3-dienes; the parallellism between the latter reaction and either the photoinduced hydrogenation of 1,3-dienes in the presence of $Cr(CO)_6$ [5] or the arenechromium tricarbonyl high temperature catalysis [6] led them to propose a common catalytic chromium tricarbonyl species.

These contradictory results * called for further investigations. We tried first

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* Recently Koerner Von Gustorf and co-workers claimed the observation of the photoinduced dissociation of one CO ligand during photolysis of 2,4-hexadienechromium tetracarbonyl in an argon matrix [7]. We fear that even if formation of monodentate I is the main process, the latter species may not be evidenced in low-temperature matrices.

to see whether preliminary *cis*-substitution could be observed when I is irradiated at low temperatures in an aliphatic glass containing triphenylphosphine. Then we investigated the rate of photoinduced conversion of I under three different sets of conditions which were: in the presence of H_2, in the presence of $P(C_6H_5)_3$ and finally in the presence of both reagents. Such comparative experiments allowed us to devise a reaction mechanism which accounts for both Darensbourgs' results, and ours, in spite of the apparent contradictions.

Results and discussion

A. Low-temperature irradiation

A deaerated aliphatic solution (decaline/methylcyclohexane, 1 : 1) of I and $P(C_6H_5)_3$, was irradiated ($\lambda > 300$ nm) at various temperatures between 77 and 200 K and the infrared spectrum was scanned periodically in the CO stretching region. At very low temperatures no reaction took place, and degradation of the complex, with formation of free carbon monoxide, occurred only after several hours intensive irradiation. Between 150 and 200 K, three bands appeared, at 1980w, 1910s and 1870s cm^{-1}, respectively, together with a small band due to $Cr(CO)_6$ and another small band at 1928 cm^{-1} which must be assigned to a thermally unstable intermediate produced from I alone *.

When the reaction mixture was allowed to warm up (Fig. 1) the 1928 cm^{-1} band decreased progressively and a weak band appeared at 1969 cm^{-1} (moving to 1966 cm^{-1} at room temperature).

Comparison of the CO stretching pattern obtained after low temperature irradiation with that obtained after room temperature irradiation [3], allows unambiguous interpretation of the results: namely that the first substituted complex formed at about 150 K is II.

The weak 1966 cm^{-1} band which was always observed in the room temperature spectrum of the analytically pure product [3] may tentatively be assigned to a small amount of the *cis* isomer (the other two expected bands being either too weak or hidden) **.

When a solution of II, containing its equilibrated amount of the assumed *cis* isomer, was cooled to about 200 K, the intensity of the small 1966 cm^{-1} band decreased; further cooling, however, never caused complete displacement of the equilibrium to the pure *trans* derivative, probably because the isomerization is too slow.

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[*] Irradiation ($\lambda > 300$ nm) of I in a deaerated aliphatic solution at approximately 170 K was accompanied by a complex change in the CO stretching pattern: in addition to $Cr(CO)_6$, more than one thermally unstable intermediate must have been formed; indeed a distinct band was observed at 1928 cm^{-1}, another was hidden under the 1960 cm^{-1} band of the parent complex, and three broad although weak absorptions were detected at 1880, 1850 and 1835 cm^{-1}. All these bands vanished when the cell was allowed to warm to room temperature, while the absorptions due to I and $Cr(CO)_6$ increased. The presence of free carbon monoxide was never detected at 150—200 K, but when the photolysed solution was subsequently cooled to 77 K, a weak band was observed at about 2130 cm^{-1}. We suspect that secondary photolysis cannot be avoided, since the ultraviolet-visible spectrum showed that low-temperature irradiation promoted an increase of optical density at all wavelengths and especially about 366 nm (maximum intensity of the lamp).

[**] The homogeneity of the crystals of II was confirmed [12].

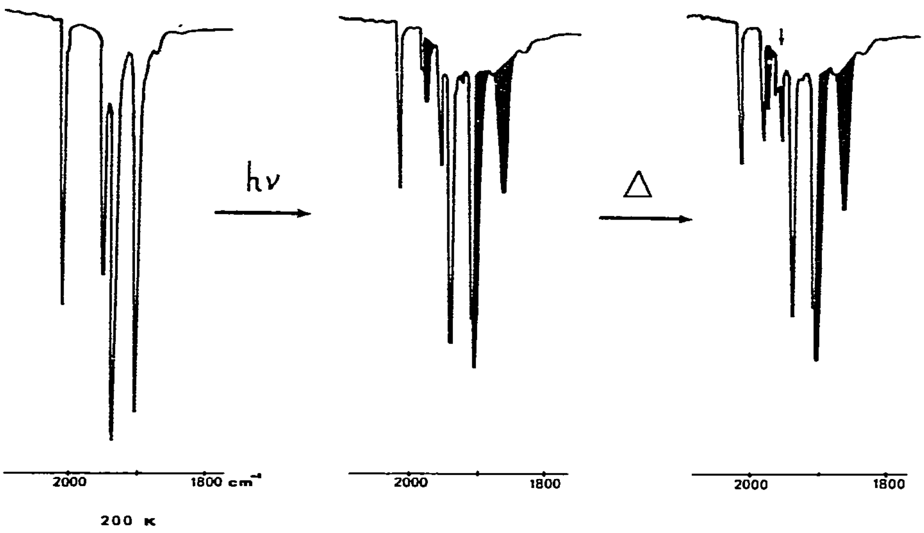


Fig. 1. Low temperature irradiation of (norbornadiene)Cr(CO)$_4$ in the presence of P(C$_6$H$_5$)$_3$ in decaline/methylcyclohexane, and subsequent thermal evolution.

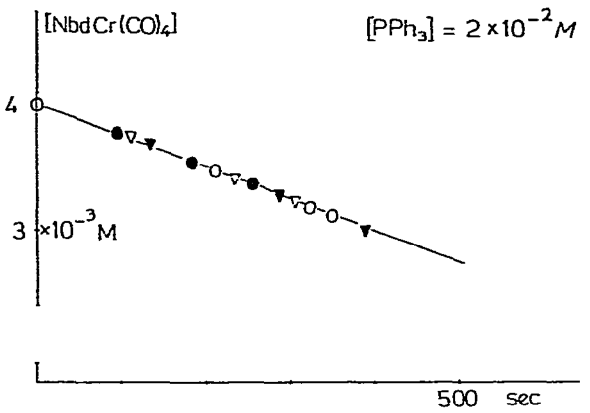
B. Quantum yields of photoinduced conversion of I in various conditions

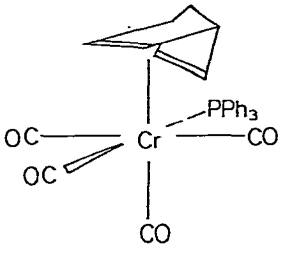
We have seen [1] that irradiation of I in an aliphatic solution saturated with H_2, yields a mixture of nortricyclene and norbornene, the chromium carbonyl moiety being degraded ultimately into Cr(CO)$_6$, metallic chromium and NbdCr(CO)$_5$. An approximate quantum yield (ϕ 0.1) was measured at 366 nm in n-pentane solution (360 torr H_2 pressure, total pressure 1 atm), using vapour-phase chromatography of the organic products as analytical tool.

Much more accurate measurements have now been done in cyclohexane solution (660 torr H_2 pressure, total pressure 1 atm) using infrared spectroscopy in the CO stretching region as analytical tool: the value thus found is ϕ 0.140. The quantum yield of photoinduced substitution at 366 nm in the presence of various amounts of P(C$_6$H$_5$)$_3$ ranging from 5×10^{-3} to 2×10^{-2} *M*, was invariably 0.105. When a solution of I 4×10^{-3} *M* in cyclohexane saturated with H_2 and containing P(C$_6$H$_5$)$_3$ 5×10^{-3} or 2×10^{-2} *M*, was irradiated at 366 nm, the quantum yield of disappearance of the parent complex was invariably 0.104, and the ratio of substitution (II) to hydrogenation was 3/2, independent of the amount of P(C$_6$H$_5$)$_3$ present in the range investigated.

The experimental results are summarized in Table 1 and a typical kinetic run is shown in Fig. 2.

Since the quantum yield of disappearance of I in the presence of both H_2 and P(C$_6$H$_5$)$_3$ is not the sum of both the quantum yields in the presence of H_2 and P(C$_6$H$_5$)$_3$ separately, we can exclude the possibility that these reagents operate separately on different photoinduced transients. Thus we assume that absorption of light leads to only one low-coordinated species A, which can react either with H_2 or with P(C$_6$H$_5$)$_3$ or revert to I. But since the quantum yield in the presence of the phosphine is the same as that in the presence of both H_2 and P(C$_6$H$_5$)$_3$, we must assume that when enough phosphine is present, hydrogen





(B)

Fig. 2. Rate of photoinduced disappearance of (norbornadiene)Cr(CO)$_4$ in the presence of P(C$_6$H$_5$)$_3$ in cyclohexane at room temperature.

Fig. 3. Transient B (Scheme 1).

does not react with A but intervenes later. Furthermore, since a fourfold increase in phosphine concentration does not alter the rate, we assume that reversal does not occur when as much as 5 × 10^{-3} *M* phosphine is present in the medium. The decrease of quantum yield with respect to the hydrogenation quantum yield measured in absence of phosphine, must then be assigned to some kind of reversal from a second intermediate B (see Scheme 1). Hydrogen does not react with transient B, since such a reaction would again lead to an increase of quantum yield going from a solution containing P(C$_6$H$_5$)$_3$ alone to a solution containing both H$_2$ and P(C$_6$H$_5$)$_3$. So we assume the existence of a third intermediate C which will then lead either to II or to the hydrogenation products.

SCHEME 1

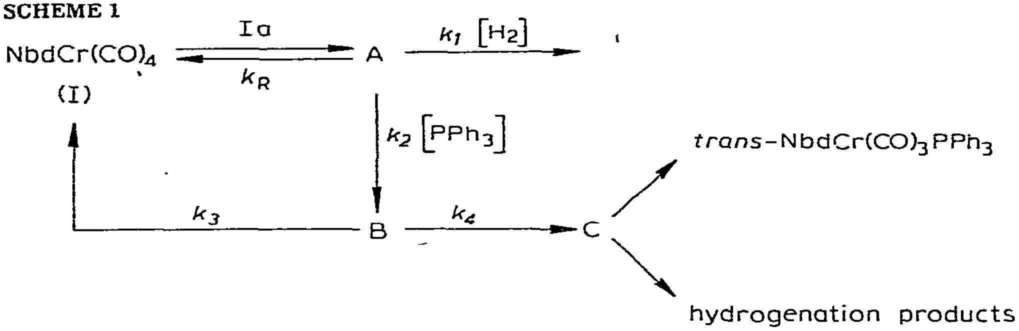


TABLE 1

CONVERSION OF NbdCr(CO)$_4$ (λ 366 nm; H$_2$ pressure 660 torr)

	H$_2$	H$_2$ + P(C$_6$H$_5$)$_3$ [a]		P(C$_6$H$_5$)$_3$
[P(C$_6$H$_5$)$_3$]		2 × 10^{-2} *M*	5 × 10^{-3} *M*	2 × 10^{-2} *M*
Quantum yield	0.140	0.104	0.104	0.105

[a] NbdCr(CO)$_3$P(C$_6$H$_5$)$_3$/hydrogenation products = 3 : 2.

If in agreement with Darensbourg and Nelson [2] we assume that A is $NbdCr(CO)_3$ with *cis* vacancy, B would be *cis*-$NbdCr(CO)_3[P(C_6H_5)_3]$, and reversal to I would consist in the bimolecular substitution of the phosphine ligand by free carbon monoxide; indeed a dissociative process would lead back to A, and we have seen that the reversal from A does not occur in the presence of enough phosphine.

However, Fig. 2 shows that the reaction is of exactly zero order. Zero order would never be observed if reversal were due to a reaction with CO, since the rate of disappearance of the parent compound would progressively decrease as the carbon monoxide concentration increases in the course of reaction *.

Thus we believe that transient A is monodentate $NbdCr(CO)_4$, which reacts with $P(C_6H_5)_3$ to form transient B, as schematically represented in Fig. 3. This crowded molecule containing a free nucleophilic site will have only a short life-time, and chelation will rapidly occur by expulsion either of $P(C_6H_5)_3$ or of CO **. If we take into account that, Darensbourg and Nelson [2] observed at room temperature, the photoinduced release of a *cis* ligand, we may conclude that C is *cis*-$NbdCr(CO)_3[P(C_6H_5)_3]$. Intramolecular substitution leading to the latter product is more probable from a statistical point of view, and also because rotation of norbornadiene needs only to be 90° from its initial position; however the activation energy may be high on account of steric interactions. On the contrary, chelation leading to II is less probable (180° rotation of the diene) but the activation energy could be lower, and this process would explain the unique formation of the *trans*-substituted derivative at 150—200 K. Alternatively the course of the reaction may be mainly determined by the entropic factor at room temperature; and this gives *cis*-$NbdCr(CO)_3[P(C_6H_5)_3]$; this is probably unstable for steric reasons; and the easiest thermal process is the opening of the chelate, allowing either isomerization to the final *trans*-$NbdCr(CO)_3[P(C_6H_5)_3]$ or hydrogenation. Scheme 2 represents the multistep reaction occurring when enough phosphine is present to avoid direct reaction of H_2 with the initial photoinduced transient. It is consistent with Scheme 1, from which the following overall rate equation has been derived, assuming steady-state concentrations for all labile chromium complexes:

$$R = \frac{I_a\phi_a\{(k_3 + k_4)k_1[H_2] + k_4k_2[PPh_3]\}}{(k_3 + k_4)\{k_2[PPh_3] + k_R + k_1[H_2]\}}$$

where ϕ_a is the quantum yield of formation of transient A.

Measurement of the rate of hydrogenation of I at various hydrogen pressures would allow the determination of k_1, k_R and ϕ_a only if there is no reversal step for the H_2 addition complex [1]. Knowing the value of ϕ_a, the ratio k_3/k_4 could be evaluated. However we are doubtful about quantitative values derived from such complex system. A rather low value of ϕ_a (<0.2) consistent with our results [9], would have to be interpreted by assuming that transient A proceeds from an excited state which relaxes very easily to the ground state, more easily

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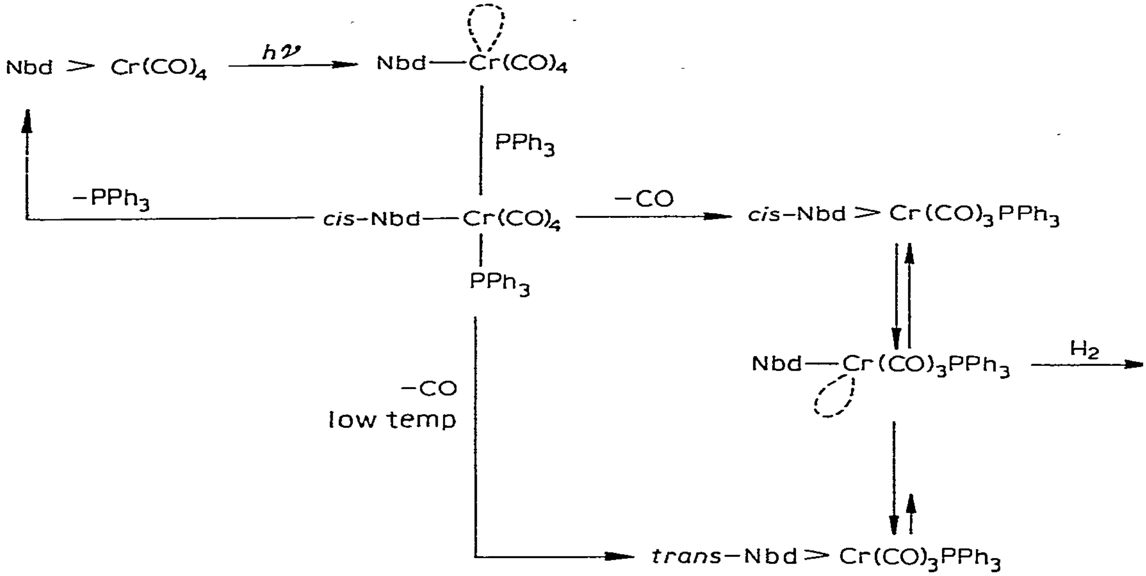
* The presence of an excess of CO would obviously lead to a decrease of quantum yield because of the reaction of CO with A, whatever A is.

** Such a chelation reaction in an intermediate of type B has recently been evidenced [8].

SCHEME 2



for example than the electronically excited chromium hexacarbonyl [10], which is known to loose carbon monoxide.

Experimental

Products

NbdCr(CO)$_4$ was sublimed before use. Triphenylphosphine: Aldrich 99.5%. Sublimed product gave identical results. Cyclohexane: Merck Uvasol. Decaline: Aldrich spectrophotometric grade, gold label. Methylcyclohexane (Hopkin and Williams) was filtered upon a silacagel column till absence of any aromatic compound.

Determination of quantum yields

The cyclohexane solutions (4×10^{-3} *M* complex) were deaerated by several freezing, pumping and thawing cycles (10^{-4} torr) then equilibrated under 1 atm total pressure with H_2 (or He for the experiments with $P(C_6H_5)_3$). Monochromatic irradiation was performed with an HPK mean pressure lamp (125 W) fitted with a Kodak filter (λ 366 nm) on an optical bench. The reaction rate was followed by withdrawing samples (80 μl) and measuring the optical density at 2035 cm^{-1} (NbdCr(CO)$_4$) and at 1870 cm^{-1} (Nbd)Cr(CO)$_3$[P(C$_6$H$_5$)$_3$]) in a 0.2 mm pathlength infrared cell. The extent of hydrogenation in the experiments in presence of $P(C_6H_5)_3$, was determined in two ways: (a) by difference between the loss of parent complex and the amount of substituted complex, (b) by measuring the 1890 cm^{-1} band of *trans*-[P(C$_6$H$_5$)$_3$]$_2$Cr(CO)$_4$ which is formed from the chromium moiety after hydrogenation; the latter complex does not precipitate from cyclohexane at low conversions. The results were in good agreement.

Actinometry was carried out using potassium ferrioxalate [11]. The low-temperature irradiations were carried out in a RIIC VLT-2 variable-temperature cell fitted with sapphire windows, using pyrex-filtered light from an HPK 125 W lamp (366 nm light gave identical results). The solution was previously deaerated by bubbling helium and was directly transferred into the He-purged infrared cell.

The spectra were scanned on a Perkin—Elmer 357 apparatus. Total absorption of the light by the parent complex during the kinetic runs, was confirmed by monitoring the ultraviolet spectra on a Unicam SP 1800 apparatus. In the experiments where $NbdCr(CO)_3[P(C_6H_5)_3]$ was formed, the latter complex absorbed a significant part of the light; however secondary photolysis occurs only after 50% conversion of the parent $NbdCr(CO)_4$ complex [3].

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