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PHOTOCHEMICAL REACTION OF NORBORNADIENECHROMIUM TETRACARBONYL WITH TRIPHENYLPHOSPHINE

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Summary

(Norbornadiene)$Cr(CO)_3[P(C_6H_5)_3]$ has been synthesized. Its infrared, ^1H and ^{13}C NMR spectra are discussed.

Introduction

The unusual photostability of norbornadienechromium tetracarbonyl in deaerated aliphatic solvents, even when it is irradiated in an open vessel, led us to the conclusion [1] that the main primary photochemical process does not consist in carbon monoxide dissociation but in metal—olefin bond rupture, followed by rapid thermal return to full coordination.

This concept was extended to the chromium tetracarbonyl complexes of non-cyclic conjugated dienes, which are effective catalysts for the photo-induced hydrogenation of the free dienes [2].

Actually, loosening of the diene chelate seems to be an assumption specially suitable in order to elucidate the peculiar behaviour of pure *cis, trans*-2,4-hexadiene (aliphatic solution) during hydrogenation, when (norbornadiene)-$Cr(CO)_4$ is used as precatalyst* [3]. Indeed, hydrogenation of the diene continues thermally at the same rate after extinction of the light as during irradiation; on the contrary, the same experiment realized with the pure *trans,trans* isomer shows that the photochemical reaction is slower and that no hydrogenation occurs in the dark. It is tempting to ascribe this marked difference to the smaller rate of thermal chelation (even if a non planar *s-cis* conformation is retained in the complex) for the sterically hindered *cis,trans* isomer, so that activation of molecular hydrogen becomes more competitive. Nevertheless, loss of

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* Very different behaviour was observed when $Cr(CO)_6$ was used as precatalyst or when mixtures of isomers were hydrogenated [2].

carbon monoxide is the most general photochemical process with arene and polyolefin metal carbonyl complexes [4]. Moreover, the photochemical formation of (norbornadiene)W$(CO)_3$Sb$(C_6H_5)_3$ and (norbornadiene)W$(CO)_3$As-$[N(CH_3)_2]_3$ from (norbornadiene)W$(CO)_4$ has been reported [5], but these complexes were not isolated and their presence was only inferred from the existence of three new carbonyl stretching frequencies in the infrared spectrum of the reaction medium.

Photodimerization of norbornadiene was observed in the presence of (norbornadiene)Cr$(CO)_4$ [6] but no intermediate could be detected. Photochemical ^{13}CO incorporation in (norbornadiene)Cr$(CO)_4$ was successful [7]; however, this could result either from a mere light-induced substitution or from a multistep process.

The analogy between, on the one hand, the thermal hydrogenation of conjugated dienes catalyzed either by (arene)Cr$(CO)_3$ [8] or by Cr$(CO)_3(CH_3CN)_3$ [9] and, on the other, their photo-induced hydrogenation in the presence of chromium carbonyl complexes [1,2,10,11] has led [9] to the conclusion that a common (diene)Cr$(CO)_3$ H_2 intermediate must be responsible for the reaction.

Because of the lack of information related to the photochemical reactions of (diene)-Group VI metal tetracarbonyls, we have initiated an investigation of the behaviour of (norbornadiene)Cr$(CO)_4$ irradiated in the presence of various ligands.

Results and discussion

A. Synthesis and structure determination

The reaction of (norbornadiene)Cr$(CO)_4$ with $P(C_6H_5)_3$ in deaerated n-pentane solution was essentially the same under polychromatic (pyrex vessel) as under monochromatic irradiation (366 nm) where the complex only absorbs the light. The substitution was monitored by scanning periodically the infrared spectrum, using a NaCl cell sealed to the photolysis cell, itself fitted with a degassing stop-cock. Progressive disappearance of the four CO stretching bands of (norbornadiene)Cr$(CO)_4$ coincided with the simultaneous appearance of four new bands at 1978w, 1966w, 1906s and 1872s cm^{-1}; thin-layer chromatography confirmed that only one substitution product, temporarily called X, was formed during the first 50% of conversion.

Subsequently, yellow crystals deposited in the reaction medium, which were identified as *trans*-$[P(C_6H_5)_3]_2$Cr$(CO)_4$ according to their strong 1890 cm^{-1} and very weak 1945 cm^{-1} absorption bands in CS_2 or CCl_4 solution [21].

X was converted into *trans*-$[P(C_6H_5)_3]_2$Cr$(CO)_4$ by heating either the crystals or a deaerated aliphatic solution at 60°C. This reaction was, however, inhibited by the presence of excess of $P(C_6H_5)_3$. Photochemical conversion of X to *trans*-$[P(C_6H_5)_3]_2$Cr$(CO)_4$ was efficient in both the presence and absence of free phosphine, the maximum yield being 50%. X which is very soluble in C_6H_6 was very rapidly destroyed by solvents such as CCl_4 or CS_2. The electronic absorption spectrum of X in pentane was characterized by a broad maximum at 458 nm (ϵ about 10^3).

The NMR spectra are shown in Figs. 1-4 and summarized in Tables 1 and

TABLE 1

^{13}C NMR SPECTRUM OF (NORBORNADIENE)Cr(CO)$_3$(PPh$_3$) in C_6D_6 SOLUTION
Internal ref. TMS.

	Chemical shifts (ppm)
C_6H_5	137.2 to 128.1 multiplet
CO	240.0 doublet; J(P—M—CO) 7.4 cps 235.8 doublet; J(P—M—CO) 20.6 cps
CH=CH	59.8 singlet and 79.5 singlet
CH	46.8 singlet
CH_2	60.1 singlet

2. Table 3 shows the influence of complexation and substitution on the chemical shifts of the norbornadiene protons.

Both ^1H and ^{13}C NMR spectra as well as elemental analysis indicate that the new complex contains one $P(C_6H_5)_3$ and one norbornadiene molecule. The problem remaining is to distinguish between a complex still having four carbon monoxide ligands and monodentate norbornadiene, or a complex having only three carbon monoxide ligands and bidentate norbornadiene. Elemental analysis being not very useful at this stage, the NMR spectra are the only tool at our disposal*.

On account of the slow spin relaxation rate of the carbonyl carbons, and in spite of very short impulses (2 or 3 μsec), it was impossible to compare the computed integration values of the signals characteristic of the various ligands. A large time delay could not be applied on account of the thermal degradation of the complex in solution. Figure 1 shows, however, that integration of the carbonyl region favours the existence of three carbon monoxide ligands.

The (norbornadiene)Cr(CO)$_3$[P(C$_6$H$_5$)$_3$] molecule can exist as two isomers I and II. Both structures I and II are consistent with the existence of two different olefinic ^{13}C resonances (59.8 and 79.5 ppm) and two different vinylic proton resonances (3.66 and 3.52 ppm). In isomer II, two equivalent carbonyl

TABLE 2

THE 270 MHz PMR SPECTRUM OF (NORBORNADIENE)Cr(CO)$_3$(PPh$_3$) in C_6D_6 SOLUTION
Internal ref. TMS.

	Chemical shifts (ppm)
C_6H_5	7.58 triplet and 7.03 to 6.93 multiplet
CH=CH^a	3.66 broad singlet and 3.52 broad singlet
CH^a	3.17 broad singlet
CH_2	0.86 and 0.68 ($J(AB)$ = 7.5 cps)

[a] The 60 MHz spectrum shows a 2.4 cps coupling constant comparable to the value observed in (norbornadiene)Cr(CO)$_4$ [13].

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[*] In the course of publication, Dr. Germain (Université Catholique de Louvain, Belgium) has confirmed by X-ray diffraction that structure I is correct.

TABLE 3

INFLUENCE OF COMPLEXATION AND SUBSTITUTION ON THE CHEMICAL SHIFTS OF THE NORBORNADIENE PROTONS

Compound	δ(CH=) (ppm)	δ(CH) (ppm)	δ(CH_2) (ppm)	Ref.
Norbornadiene	6.73	3.57	1.98	12
(Norbornadiene)$Cr(CO)_4$	4.36	3.66	1.30	13
(Norbornadiene)$Cr(CO)_3P(C_6H_5)_3$	3.66 and 3.52	3.17	0.86 and 0.68	this work

groups are *cis* to the phosphorous atom and one is *trans* to it. If this structure is assumed, the value of the coupling constants, i.e. 20.6 Hz for the more intense doublet and 7.4 Hz for the less intense doublet, contradict the reported values for tungsten and molybdenum complexes [14,16] where *J*(P—M—*trans*-

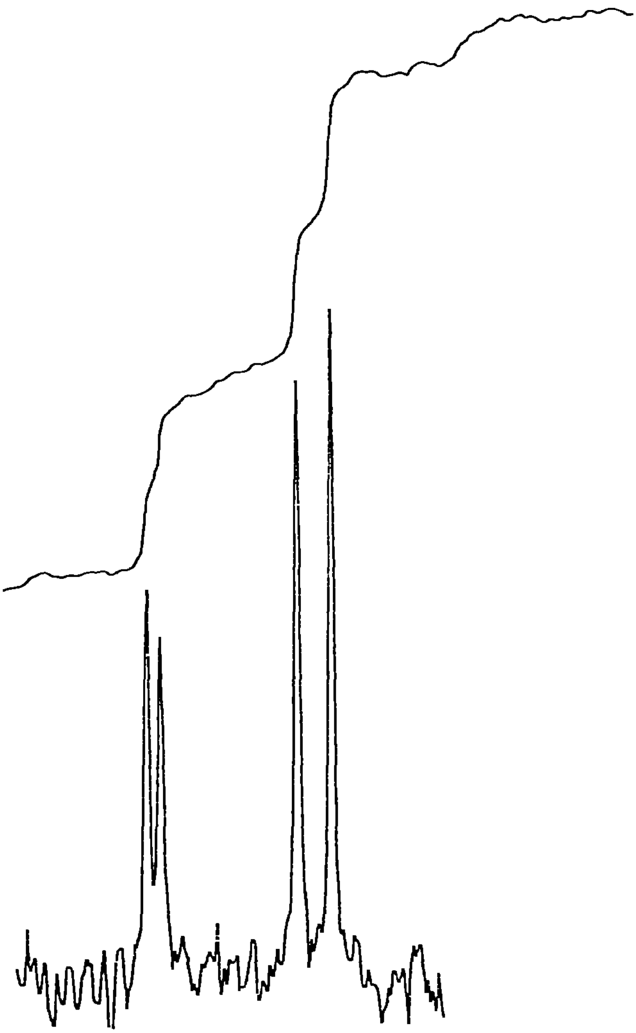
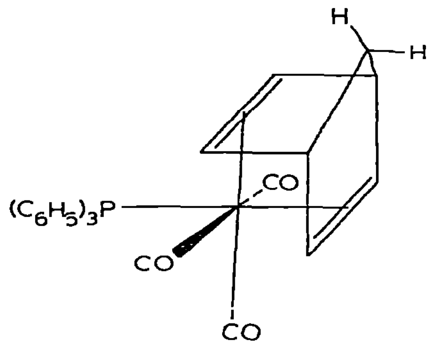
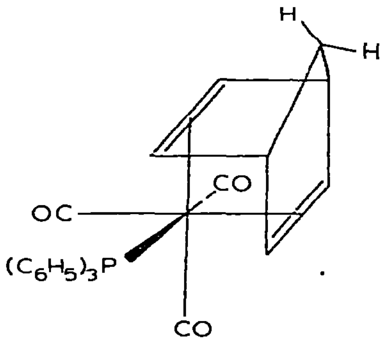


Fig. 1. ^{13}C NMR spectrum of (norbornadiene)$Cr(CO)_3(PPh_3)$ in C_6D_6 showing the CO resonance and integration.



(I)



(II)

CO) > *J*(P—M—*cis*-CO). Moreover, the proton NMR spectrum presents a well defined *AB* system for the methylene protons while the resonance of the allylic protons shows them to be equivalent, and this situation is in agreement with structure I only.

Although it is difficult to account for the existence of two very different *J*(P—M—CO) values since all three carbon monoxide ligands are *cis* to the phosphorus atom in structure I, this structure seems more plausible.

The question arises now as to the existence of four carbonyl stretching modes (see Fig. 5). Obviously both structures I and II would allow only three

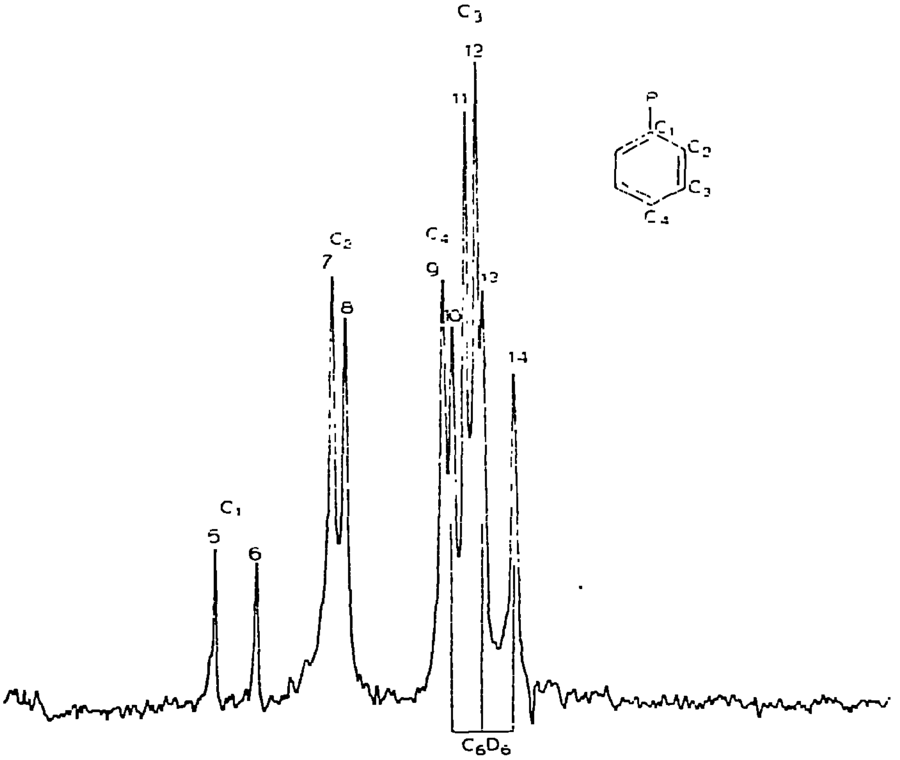


Fig. 2. ^{13}C NMR spectrum of (norbornadiene)Cr(CO)$_3$(PPh$_3$) in C_6D_6 showing the phenyl resonance.

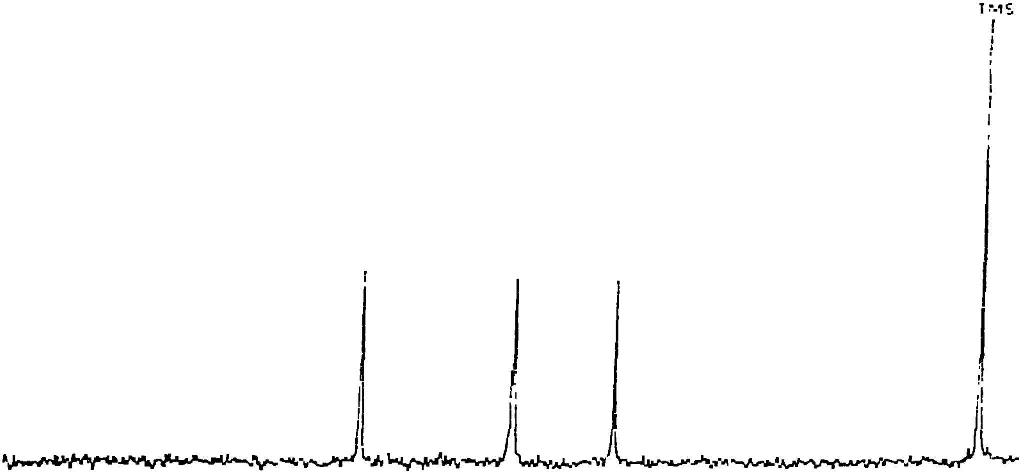


Fig. 3. ^{13}C NMR spectrum of (norbornadiene)$Cr(CO)_3(PPh_3)$ in C_6D_6 showing the norbornadiene resonance.

absorption bands. The complete infrared spectrum, scanned using a Nujol mull, permits the possibility that one band is an overtone of a strong fundamental mode near 1000 cm^{-1} to be discounted; as expected, the pattern of the carbonyl stretching region is very badly resolved under such conditions. Some anomalies in the infrared spectra of metal carbonyls have been reported recently [15] which show that $P(OR)_3$ and $P(C_6H_5)_3$ ligands lead to the existence of an

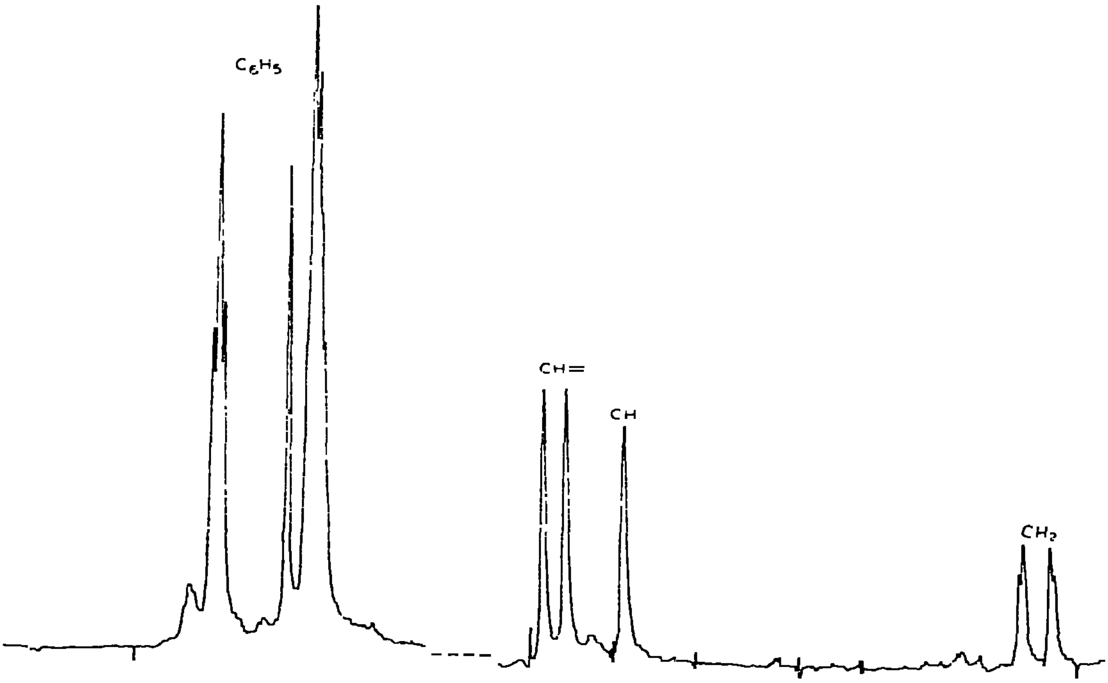


Fig. 4. 270 MHz ^1H NMR spectrum of (norbornadiene)$Cr(CO)_3(PPh_3)$ in C_6D_6.

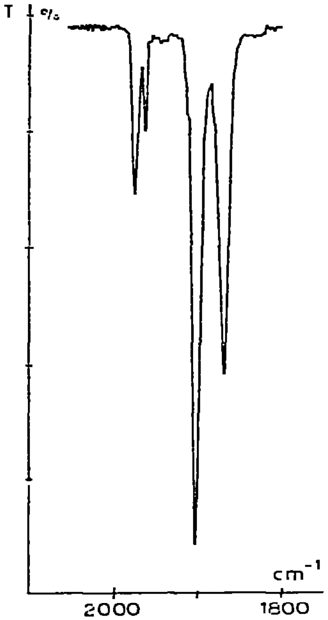


Fig. 5. IR spectrum of (norbornadiene)Cr(CO)$_3$(PPh$_3$) in n-pentane.

excess of carbonyl stretching bands. The presence of two or more conformers resulting from restricted rotation about the P—O or P—C bonds, is generally proposed. Occurrence of a similar phenomenon in the case of (norbornadiene)-Cr(CO)$_3$[P(C$_6$H$_5$)$_3$] is possible; more detailed variable temperature infrared and NMR experiments could be explicit in this respect and would facilitate better understanding of the carbonyl ^{13}C resonance peaks. Unfortunately, this is a tedious program on account of the instability of the complex in solution, especially in presence of traces of air.

B. Evaluation of the photochemical stability of (norbornadiene)Cr(CO)$_3$ in the presence of potential ligands

Preliminary experiments with tetrahydrofuran 10^{-1} *M* in n-pentane solution showed that prolonged irradiation promoted only very slight destruction of the (norbornadiene)Cr(CO)$_3$ complex.

The rates of photoinduced disappearance of (norbornadiene)Cr(CO)$_3$ 1.7 × 10^{-3} *M* in presence either of P(C$_6$H$_5$)$_3$ or of molecular hydrogen in n-pentane solution, were measured under the same conditions (366 nm where the complex absorbs 100% of the light). Comparison was restricted to low conversion yields, i.e. almost zero order reaction. The rate observed with P(C$_6$H$_5$)$_3$ 9 × 10^{-3} *M* and 0.9 × 10^{-3} *M* was similar to the rate of hydrogenation of (norbornadiene)Cr(CO)$_3$ under 360 Torr H$_2$ (i.e. about 2 × 10^{-3} *M*), the corresponding quantum yield being approximately 0.1 [1]. Thus it looks as if photoinduced hydrogenation occurred with the same efficiency as loss of carbon monoxide and as if CO dissociation could be rate determining during the hydrogenation of the complex. This assumption is, however, premature since, if we as-

TABLE 4

REACTIONS OF (ARENE)METAL AND (POLYENE)METAL CARBONYL COMPLEXES

Reactants	Conditions	Product	Ref.
(Arene)$Cr(CO)_3$ + PR_3	hν	(Arene)$Cr(CO)_2PR_3$	4
(Cycloheptatriene)$Cr(CO)_3$ + PR_3	hν	(Cycloheptatriene)$Cr(CO)_2$ PR_3	17
(Norbornadiene)$Cr(CO)_4$ + PR_3	hν	(Norbornadiene)$Cr(CO)_3PR_3$	this work
(Arene)$Cr(CO)_3$ + PR_3	Δ	$(PR_3)_3Cr(CO)_3$	18
(Cycloheptatriene)$Cr(CO)_3$ + L	Δ	$L_3Cr(CO)_3$	19
(Norbornadiene)$Cr(CO)_4$ + PR_3	Δ	$(PR_3)_2Cr(CO)_4$	20

sume a competition between reaction of the low-coordinated intermediate with a potential ligand (phosphine or molecular H_2) and recombination with CO, direct comparison of our preliminary experiments is meaningless. Actually, recombination with CO (which looks so fast on account of the high photostability of (norbornadiene)$Cr(CO)_4$ in pure aliphatic solution) ought to prevent the photoinduced reaction from being zero-order when low free ligand concentrations are used.

Moreover, the exact mode of action of the phosphine must be determined.

Very accurate quantum yield determinations in wide ranges of phosphine and hydrogen concentrations would be needed to allow any discussion of the nature and efficiency of the primary photochemical process(es) in (norbornadiene)$Cr(CO)_4$.

From a practical standpoint it is interesting to note that (norbornadiene)-$Cr(CO)_4$ seems to give rise, respectively by photo- and thermal-induction, to the same kind of reactions with phosphine as (arene)$Cr(CO)_3$ and (cycloheptatriene)$M(CO)_3$ complexes; Table 4 summarizes these experimental results.

Experimental

Synthesis

A deaerated (N_2-stream) solution of 1 g (norbornadiene)$Cr(CO)_4$ and 0.68 g $P(C_6H_5)_3$ (Aldrich, 99% purity) in 250 ml aromatic-free petroleum ether (60-90°), was irradiated with a HPK mean pressure lamp (125 W) in a pyrex vessel for 1 hour. A small amount of *trans*-$[P(C_6H_5)_3]_2Cr(CO)_4$ was removed by filtration and the solution concentrated under reduced pressure to ca. 10 ml whence red crystals formed. Several washings of the precipitate with petroleum ether were necessary to remove the initial products completely, but perfectly pure (norbornadiene)$Cr(CO)_3[P(C_6H_5)]_3$ was thus obtained in 50% yield. Elemental analysis: found: C, 68.56, H, 4.92, P, 6.95. $C_{28}H_{23}CrO_3P_3$ calcd.: C, 68.57, H, 4.73, P, 6.31%.

Purification of the product by chromatography on silica gel, using a petroleum ether/diethyl ether (90/10) mixture as eluent, is less efficient than mere washings because of degradation on the column.

Preparation of (norbornadiene)$Cr(CO)_3[P(C_6H_5)]_3$ was attempted by irradiation (366 nm) of $P(C_6H_5)_3Cr(CO)_5$ in presence of norbornadiene in an aliphatic solvent, but the infrared analysis, recorded periodically, showed that (norbornadiene)$Cr(CO)_4$ was formed first and was probably the true antecedent of small amounts of (norbornadiene)$Cr(CO)_3[P(C_6H_5)]_3$ formed in such conditions. Other complexes such as $Cr(CO)_6$ and *trans*-$[P(C_6H_5)_3]_2Cr(CO)_4$ were also detected.

Attempts to use (norbornadiene)$Cr(CO)_3[P(C_6H_5)_3]$ as a hydrogenation catalyst for norbornadiene in n-pentane solution, saturated with H_2, failed on account of the destruction of the complex and formation of *trans*-$[P(C_6H_5)_3]_2$-$Cr(CO)_4$.

Apparatus

The infrared and ultraviolet-visible spectra were scanned on a Perkin—Elmer 357 and a Unicam SP 1800 respectively.

The ^{13}C NMR spectra were recorded on a Bruker HX 90 operating in the Fourier transform mode at 22.64 MHz. Proton noise decoupling was performed with the use of a 90 MHz broad band decoupler. Pulse lengths were 5, 3 and 2 μsec. The average sample temperature was 35°.

The PMR spectra were obtained on a Bruker HX 270.

Determination of photoreaction rates

n-Pentane P.A. (U.C.B.) was used as solvent. The solutions were deaerated by several freezing, pumping and thawing cycles (10^{-4} Torr).

Monochromatic irradiation was performed with an HPK mean pressure lamp (125 W) fitted with a Kodak filter (λ 366 nm) on an optical bench. When necessary, results were corrected for the slight light-absorption by the reaction product.

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