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IR LASER PYROLYSIS AND THE ISOTOPIC LABELLING OF ORGANOMETALLIC COMPOUNDS

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Summary

A homogeneous gas phase pyrolysis technique involving SF_6 sensitization and a continuous wave (CW) CO_2 laser, is described for preparing small quantities (~ 100 mg) of organometallic compounds. Several reactions have been successfully carried out and the synthesis of $Os(CO)_5$ from $H_2Os(CO)_4$ and CO is discussed in detail. With IR laser pyrolysis, room temperature reactors and sub-atmospheric pressures can be used for reactions which normally require high pressures and temperatures.

Introduction

Although lasers have played a central role in unravelling the photochemistry of organometallic compounds [2], their impact on synthetic organometallic chemistry has been limited. The pioneering experiments by Koerner von Gustorf [3] on laser assisted metal vapour synthesis have never been widely exploited, apart from elegant spectroscopic studies of gas phase metal clusters [4]. More generally, it is surprising that the enormous research effort which has been put into IR laser-induced chemistry [5,6] has led to very few convenient syntheses involving lasers *. In this paper, however, we show that IR lasers can indeed be useful in organometallic synthesis and describe simple preparations of otherwise awkward compounds, particularly isotopically enriched species where conventional syntheses may be impracticable.

Our approach has been to develop the technique of IR laser pyrolysis, originally devised by Shaub and Bauer [7], and Riley [8]. As used here, the method involves a continuous wave (not pulsed) CO_2 laser operating in the 950–940 cm^{-1} region and a gaseous reaction mixture to which ~ 10 Torr of SF_6 has been added as a chemically

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* Apart from the use of IR lasers to produce isotopically enriched samples (e.g. ^{34}S from SF_6), the most important preparations involving IR lasers are (i) $B_{20}H_{16}$ by laser pyrolysis of B_2H_6 [18] and (ii) the removal of $COCl_2$ impurities from BCl_3 by CW CO_2 laser pyrolysis [19]. Using the apparatus shown in Fig. 3, up to 4 g of BCl_3 can be purified in ~15 min [20].

TABLE 1

PRODUCTS PREPARED BY IR LASER PYROLYSIS [a]

Product	Reactants
$Os(CO)_5$	$(CH_3)_2Os(CO)_4 + CO$ $H_2Os(CO)_4 + CO$
$Os(^{12}CO)_{5-x}(^{13}CO)_x$ [b]	$Os(CO)_5 + {}^{13}CO$
$Fe(^{12}CO)_{5-x}(^{13}CO)_x$ [b]	$Fe(CO)_5 + {}^{13}CO$
$HMn(^{12}CO)_{5-x}(^{13}CO)_x$ [b,c]	$HMn(CO)_5 + {}^{13}CO$
$Fe(CO)_{5-x}(PF_3)_x$ $(x = 1-4)$ [b,d]	$Fe(CO)_5 + PF_3$
$Fe(CO)_3(C_4H_6)$	$Fe(CO)_5 + C_4H_6$
$Os(CO)_3(C_4H_6)$ [e]	$Os(CO_5) + C_4H_6$
$Fe(CO)_2(NO)_2$	$Fe(CO)_5 + NO$

[a] For reaction conditions see text. [b] The degree of enrichment depends on irradiation time, and appears to be statistical. [c] For a detailed discussion of the spectra of this compound see Ref. 21. [d] Identified by comparison with IR spectra [22]. [e] Identified by comparison of ν(C–O) (2080, 2008 and 2000 cm^{-1}, gas phase) with that of $(C_4H_6)Fe(CO)_3$ (2068, 2007 and 1995 cm^{-1}) and from published solution IR spectra [23].

inert photosensitizer. The SF_6 absorbs the IR radiation, there is rapid vibrational → translational relaxation, the temperature rises and thermal reactions occur in the gas mixture. Unlike conventional heat sources the IR laser heats the gases directly, while the cell walls remain relatively cool, thus minimizing product decomposition. Both experiments [7,9] and numerical modelling [9] have shown that even modest laser power can produce temperature rises of several hundred degrees centigrade, more than enough to promote substitution and exchange reactions in organometallic compounds *.

Results

We have prepared a variety of compounds of Fe, Os and Mn using IR laser pyrolysis, see Table 1. These compounds are not easily prepared photochemically in the gas phase because of facile formation of polynuclear byproducts, while the thermal syntheses are often inefficient or involve high pressures.

The synthesis of $Os(CO)_5$ illustrates the advantages of IR laser pyrolysis over more conventional preparative techniques. The usual synthesis of $Os(CO)_5$ involves the high pressure reaction of OsO_4 [11] or $Os_3(CO)_{12}$ [12] with CO, which is not really feasible with expensive isotopically labelled gases e.g., ^{13}CO. It has also been reported [13] that $Os(CO)_5$ can be obtained by the thermal pyrolysis of $(CH_3)_2Os(CO)_4$ in THF solution under high CO pressures but the reaction is slow because the alkyl compound is remarkably stable [14].

$$(CH_3)_2Os(CO)_4 + CO \xrightarrow[120°C,\ 12\ h]{CO,\ 130\ atm,\ THF} Os(CO)_5 + C_2H_6$$

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* IR laser pyrolysis using SF_6 sensitization and a pulsed CO_2 laser has been elegantly exploited by Smith and co-workers to measure bond dissociation energies for metal carbonyls [10].

By contrast using the IR laser, $(CH_3)_2Os(CO)_4$ can be smoothly converted into $Os(CO)_5$ with 0.2 atm CO and only a few minutes laser irradiation.

$$(CH_3)_2Os(CO)_4 \xrightarrow[SF_6\ 10\ Torr,\ IR\ laser]{CO,\ 0.2\ atm} Os(CO)_5$$

Unfortunately, $(CH_3)_2Os(CO)_4$ is not sufficiently volatile for large scale preparations and we have found $H_2Os(CO)_4$ (prepared from $Os_3(CO)_{12}$ in high yield [15]) a more convenient starting material *. The reactor described below (Fig. 3) can be used to prepare $Os(CO)_5$ on ~ 50–100 mg scale, virtually free from $H_2Os(CO)_4$ contamination with > 80% yield. The synthesis is considerably more efficient than the conventional route and involves neither OsO_4 nor high pressure reactors, both of which have associated health and safety problems.

The laser pyrolysis is chemically interesting because the thermal pyrolysis of $H_2Os(CO)_4$ in the presence of CO yields $H_2Os_2(CO)_8$ as the primary reaction product [16,17].

$$H_2Os(CO)_4 \xrightarrow[130°C,\ 30\ min]{CO,\ 0.4\ atm,\ mesitylene} H_2Os_2(CO)_8$$

The reasons for the difference are not clear and it may be that polynuclear osmium compounds are transiently formed during laser pyrolysis.

The technique

General procedure

The viability of each reaction was tested on a small scale using a vertically mounted cylindrical gas cell (4 cm long, 2 cm diameter) fitted with NaCl windows **. The CW CO_2 laser beam was focussed upwards into the centre of the cell (Fig. 1), an optical arrangement which promotes convection currents ***. The combination of laser-induced temperature gradients and convection currents causes rapid heating and cooling of the molecules which, it has been suggested [9], may open up reaction channels inaccessible by conventional pyrolysis. The reaction progress can be monitored at intervals using conventional IR spectroscopy (Fig. 2). A typical gas mixture of 2/12/200 Torr of $M(CO)_x/SF_6/L$ takes 2–4 min for complete reaction.

Preparative scale pyrolysis was undertaken in a mechanically pumped circulating cell designed and built in Nottingham, (Fig. 3). This cell allows IR spectra to be run continuously during laser irradiation. The vacuum taps are so arranged that the condensible products can be removed from the trap, *T*, while retaining the bulk of the non-condensable gas in the system. Thus, the same sample of ^{13}CO gas can be used for several reactions one after another.

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* Presumably the other product of the reaction is H_2 but we have not identified it conclusively. However, apart from $Os(CO)_5$, no products condensable at 77 K are formed.

** Care must be taken on the choice of window seals, since the reactants or products can be highly soluble in some greases and waxes. We recommend UV-polymerized methyl methacrylate, e.g. "Loctite Glassbond", although this decomposes $HMn(CO)_5$ catalytically.

*** These convection currents have been studied in detail [7] and IR laser pyrolysis is one of the few chemical processes where the orientation of the reaction vessel effects the outcome of the reaction [7].

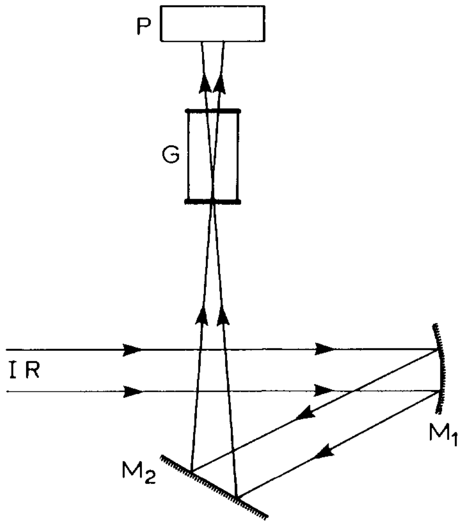

Fig. 1. Optical arrangement for small scale reactions. The IR laser beam, ~ 0.5 cm diameter, is focussed by a concave mirror, M_1, and plane mirror, M_2, onto the gas cell, G. The focal length of M_1 is not critical (10–30 cm) but shorter focal lengths tend to crack the windows less frequently. It is convenient to have a power meter, P, to check the laser output.

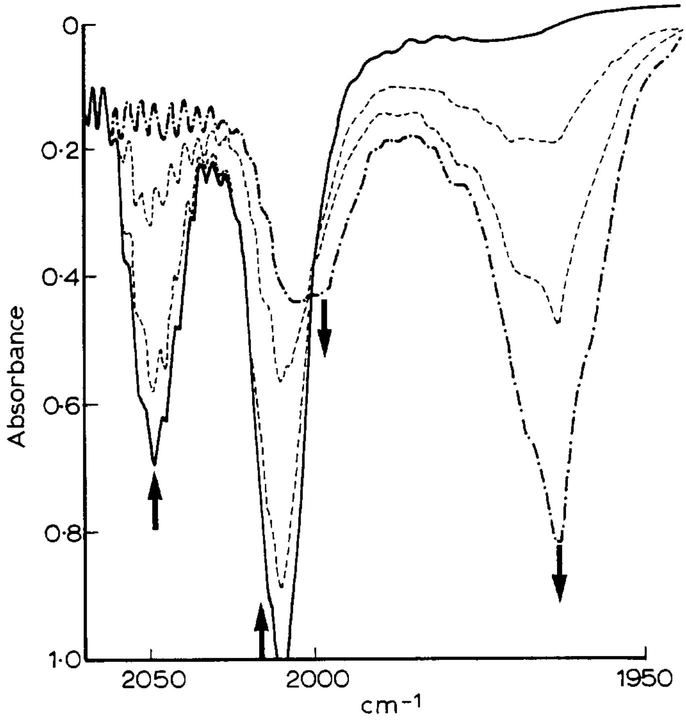

Fig. 2. ^{13}CO enrichment of $Os(CO)_5$. IR spectra taken before (———), during (------) and after (–·–·–·) 4 min IR laser irradiation (500 mW, P(20) CO_2 laser line, 944.2 cm^{-1}), using an arrangement similar to Fig. 1. The laser pyrolysis was stopped while each spectrum was run. Note the change in wave-number scale in the spectrum at 2000 cm^{-1}.

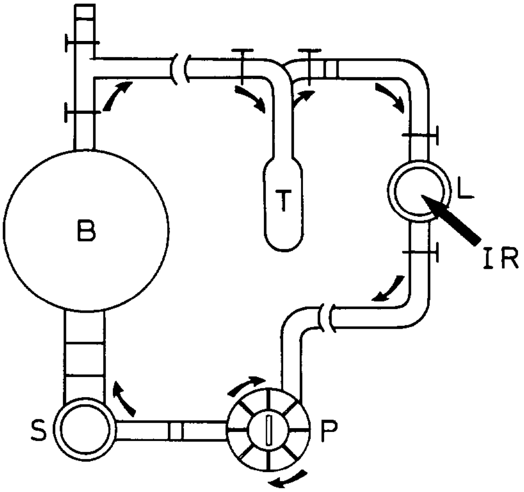

Fig. 3. Glass apparatus for preparative scale IR laser pyrolysis. L is the laser irradiation cell; S the spectroscopic cell for monitoring the reaction; P is a glass "paddle-wheel" circulating pump, driven by an external magnetic stirrer motor; B is a 1 l glass bulb and T is a trap for condensing the products. The total volume is ~ 1.5 l, sufficient to prepare the compounds in Table 1 on a 50–100 mg scale. The apparatus can be modified to allow laser irradiation of the gas mixture in the centre of the bulb, B.

Laser requirements

The preparations can be carried with a relatively unsophisticated CW CO_2 laser. Pyrolysis is almost equally efficient on the P(16), P(18), P(20) or P(22) laser lines (947.7 to 942.4 cm^{-1}) but the laser frequency and power must be stable on the timescale of the irradiation (i.e. ~ 1 h for the large reactor). Most importantly, the laser must have a stable Gaussian beam profile (i.e. operate on TEM_{00}) to prevent local hot spots developing [20]. The laser powers required are in the range 0.5–4 W and should be variable. During irradiation the laser power is gradually increased until the reaction proceeds at a convenient rate. Further increases in power usually leads to decomposition and the formation of metallic mirrors or filaments. We have used both a home built laser [20] and an Edinburgh Instruments WL-4 waveguide CO_2 laser, which is particularly convenient because it is only 40 cm long and does not require high voltage power supplies.

Reaction conditions

We have studied the reaction of $Fe(CO)_5$ with butadiene systematically and have found that the reaction conditions are not critical and acceptable yields can be achieved over a wide range of reactant pressures. Our general conclusion are:

1. The amount of reaction is roughly proportional to irradiation time.
2. Larger volume reactors require somewhat higher laser powers.
3. Reaction rates increase with pressure of added SF_6 up to ~ 10 Torr *. Further increases in pressure make little difference.
4. Decomposition of the carbonyl increases with pressure of $Fe(CO)_5$. Up to 10

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*At these pressures the IR cell is totally absorbing at the laser wavelength and nearly all of the laser energy is absorbed by the gas close to the entrance window. Note that the IR spectrum of SF_6 is temperature dependent [9] and care must be taken when predicting the exact amount of absorption of laser light on the basis of a room temperature IR spectrum.

Torr can be conveniently used. Decomposition is partially suppressed by addition of CO.

5. A substantial excess of butadiene ~ 100 Torr is required for the best results. Similar results have been found for the other reactions in Table 1.

Safety note. Salt windows can crack unpredictably under laser irradiation and preparations are best carried out in a fume hood.

Experimental

$H_2Os(CO)_4$ was prepared [15] by Na reduction of $Os_3(CO)_{12}$ in liquid NH_3, followed by acidification with H_3PO_4 (85%). We are grateful for gifts of $Os_3(CO)_{12}$ from Professor J. Lewis and $(CH_3)_2Os(CO)_4$ from Professor J.R. Norton. $Fe(CO)_5$ (Fluorochem), SF_6 (BDH), Butadiene (BDH), CO (BOC Research Grade) and ^{13}CO (BOC Prochem) were used without further purification. All spectra were recorded on a Perkin–Elmer Model 283B IR spectrometer.

Conclusion

IR laser pyrolysis is a very promising technique. We have shown in this paper that reactions can be carried out at much lower pressures than are employed in more conventional reactors, and often with higher yields. It is now possible to prepare very quickly small quantities of isotopically enriched molecules, which were previously tedious or expensive to obtain. This will have an important effect on spectroscopic and mechanistic studies. At the moment the laser induced reactions are limited to the gas phase but preliminary experiments suggest that a CO_2 laser can also be used for flash pyrolysis of less volatile compounds. The apparatus is not expensive. A modern low power CO_2 laser costs less than a high pressure autoclave and many laboratories will already have suitable lasers.

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