(9) The complete solution to the cyclopropene mechanism is too complex to present here in detail and is delayed until a full paper. However, it takes explicit account of the intermediacy of both cyclopropene-*1-d*$_1$ (**4**) and cyclopropene-*3-d*$_1$. It also incorporates their relative propensities to shift H(D) and undergo degenerate rearrangement and all steps are considered potentially reversible. The particular ratio $k_{1,2}/k_{1,3}$ is given by $k_{1,2}/k_{1,3} = r_2/[r_1(1 + r_1 + r_2 + \alpha r_2)]$ where $r_1 = k_{4,3}/(k_{4,1} + k_{4,2})$ (Scheme II); r_2 = the relative propensity of the intermediate prop-1-ene-1,3-diyl biradical to reclose relative to H shift forming propyne; and $\alpha = k_H/k_D$, the primary kinetic isotope effect for all 1,2-H(D) shifts (secondary isotope effects being neglected).

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Total Internal Reflection Raman Spectroscopy as a New Tool for Surface Analysis

Sir:

Attenuated total reflection infrared spectroscopy (ATR IR) has been established as a standard method for characterizing material surfaces.[1-5] The surface layer observable by the method, however, is fairly deep and far from such a thin surface layer that may control surface-sensitive properties. The penetration depth of the evanescent wave on total reflection is proportional to the wavelength of the incident light.[6] The wavelength of lasers (e.g., Ar 0.4880 μm) usually used for Raman spectroscopy is much shorter than those of infrared radiations (2.5–25 μm) concerned in infrared spectroscopy. Therefore, total internal reflection laser Raman spectroscopy, which deals with scattered light from the evanescent wave of a laser penetrating the sample, should give useful information on much thinner surface layers.

Applicability of total internal reflection to Raman spectroscopy was hinted by Harrick and Loeb.[7] Ikeshoji et al.[8] measured total internal reflection Raman spectrum of CS_2, by using a flint glass as the internal reflection element (IRE). The Raman signals were so weak and obscure that they needed time averaging of signals in real time and subsequent smoothing of the obtained spectra. Their failure to obtain distinct spectra seemed to be mainly due to the background of the IRE, for the low level of background is crucially important for recording the possibly very weak signals. We began to select a suitable material for the IRE to study feasibility of the total internal reflection Raman spectroscopy as a new tool for surface analysis, and found that the method is promising.

Sapphire has the least Raman background in the 800–1800-cm^{-1} range among the candidate materials with a refractive index >1.7, including flint glasses, TiO_2, and $SrTiO_3$. All the Raman peaks of sapphire that have a considerable intensity are located below 760 cm^{-1} and the background in the 800–3100-cm^{-1} range was <200 counts per second (cps) in the ordinary conditions, and sapphire was found the most appropriate for the IRE. Sapphire was cut into a plate with a side view of trapezoid, possessing 45 and 90° end face angles and the dimension 30 (*c* axis) × $\underline{10}$ × 1 mm, the surface for contact with a sample being the (10$\bar{1}$0) plane. All the surfaces a laser beam hits were optically polished. The surface roughness was <λ/10.

Samples with a thin layer coating were prepared by coating polystyrene in various thicknesses on polyethylene films of 30-μm thickness. The polystyrene side of the sample was kept contacted intimately with the IRE surface with an appropriate pressure. The laser beam fell on the 45° end face of the IRE so that the refracted beam was incident onto the IRE–sample interface at an angle larger than the critical angle. The Raman scattering on total reflection was collected to the direction perpendicular to the IRE plate surface. The incident angle of laser onto the IRE–sample interface was varied from 68.5 to 64.8°, the latter being the critical angle for sapphire and polystyrene with a refractive index of 1.775[9] and 1.606,[9] respectively.

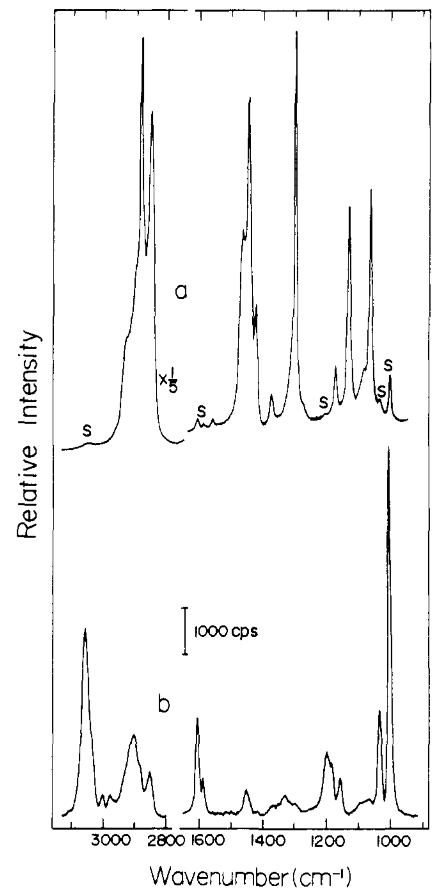

Figure 1. Raman spectra of a 30-μm-thick polyethylene film with an 1.1-μ-thick coating of polystyrene, measured by (a) illumination through the sample and (b) total internal reflection on the coated surface at an incident angle of 64.8°. The peaks marked S are due to polystyrene in the upper spectrum.

A laser Raman spectrometer used was Spex Ramalog 5 equipped with a Coherent Radiation argon ion laser CR-3 and a RCA-C31034 cooled photomultiplier. Total internal reflection Raman spectra were typically recorded with a 0.1- or 0.2-cm^{-1} s scanning speed, a time constant of 10 or 20 s, a 10-cm^{-1} slit width, and 200-mW laser power at 488.0 nm. The total internal reflection Raman spectra were measured on a single total reflection. The diameter of the laser beam was ~0.1 mm at the site of the total reflection.

The Raman spectrum measured by the conventional illumination through the polyethylene film with an 1.1-μm-thick coating of polystyrene (Figure 1a) shows several weak but distinct peaks due to polystyrene, the peak at 1002 cm^{-1} being the most intense of all the polystyrene peaks, in addition to predominant polyethylene peaks. Figure 1b is the total internal reflection Raman spectrum on the coated surface of the same sample. All the peaks therein are of polystyrene and even the strongest peaks of polyethylene at 2850 and 2890 cm^{-1} do not appear, showing striking contrast with the conventionally measured spectrum (Figure 1a). A total internal reflection

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Raman spectrum on as thin coating layer as 0.05 μm or less showed five peaks of polystyrene, which were sufficiently well defined for their identification separately from those of polyethylene, while the conventional Raman spectrum of the same sample was completely of polyethylene, the 1002-cm^{-1} peak of polystyrene being hardly observed.

The observed facts meet the expectation that the method can be applied to analysis of much thinner surface layers than ATR IR. The present study is the first to demonstrate powerfulness of the total internal reflection laser Raman method for surface analysis by molecular species.[10] Details of the present study will be published in the near future.

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(10) The doubt if the obtained Raman spectra might be attributed to the scattered light caused by surface roughness at the IRE interface was completely denied by systematic measurements on two-layered samples of polystyrene and polycarbonate (11.5 μm thick), thickness of the polystyrene layer varying from 0.013 to 0.93 μm, in the range of the incident angle from θ_c to θ_c + 5.0° (θ_c = critical angle). The details will be published elsewhere in the near future.

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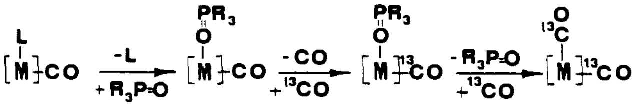
Synthesis of Metal Carbonyl Complexes Highly Enriched in Carbon-13: Utilization of the CO-Labilizing Ability of (n-Bu)$_3$P=O

Sir:

The carbon-13 nuclide provides a versatile spectroscopic handle for organometallic compounds (in particular, metal carbonyl derivatives) and, as such, many mechanistic studies benefit greatly from the use of ^{13}C isotopically enriched compounds. In addition, the structures of a variety of unstable metal carbonyl fragments (intermediates) have been determined by means of vibrational analysis of these species which are derived from parent carbonyl derivatives enriched in ^{13}CO to varying degrees.[1] Although a few metal carbonyl compounds exchange carbon monoxide ligands with free ^{13}CO under rather mild conditions [e.g., $Ni(CO)_4$], most undergo this ligand exchange process reluctantly. Therefore, in order to prepare ^{13}CO-enriched derivatives, methods for activating CO dissociation, such as irradiation[2] or surface catalysis involving palladium on charcoal,[3] must be employed. An alternative method for providing ^{13}C-enriched species involves replacement of a labile ligand by ^{13}CO.[4] In this communication we describe a convenient synthesis of some common starting materials, $M(CO)_6$ (M = Cr, Mo, W) and $Fe(CO)_5$, enriched in carbon-13 up to levels of >90%.

While investigating ligand exchange reactions of (CHT)-$Cr(CO)_3$ (CHT = cycloheptatriene), it was observed that mixtures of (CHT)$Cr(CO)_2(^{13}CO)$ and $Cr(^{12}CO)_3(^{13}CO)_3$ were obtained from refluxing solutions of the parent compound in hexane under a ^{13}CO atmosphere (free ^{13}CO-to-metal complex molar ratio ~50:1). Under these conditions CHT replacement by ^{13}CO was much more facile than CO exchange. With the addition of large excesses of (n-Bu)$_3$P=O (the phosphine oxide to metal ratio was ~30:1 for convenient reaction times and the enrichment levels reported here)[5] to the reaction, however, CHT was partially or completely replaced by the phosphine oxide [ν(CO) observed for (η^4-CHT)-Cr[(n-Bu)$_3$P=O]$(CO)_3$ 1981, 1917, and 1895 cm^{-1} and for [(n-Bu)$_3$P=O]$_3$Cr$(CO)_3$ 1908 and 1783 cm^{-1}][6] yielding complexes which were very CO labile as well as ligand labile. An infrared monitor showed, for example, the buildup of [(n-Bu)$_3$P=O]$_3$Cr$(^{13}CO)_3$ prior to phosphine oxide replacement to yield $Cr(^{13}CO)_6$ in >80% spectroscopic yield. The level of ^{13}CO content in the hexacarbonyl thus obtained was found to be consistent with the level of enrichment of the free CO gas used (93.3% ^{13}CO, Prochem., Ltd.) by means of quantitative infrared analysis[4] and by a quantitative comparison of the ^{13}C NMR of the ^{13}C-enriched $M(^{13}CO)_6$ vs. natural-abundance ^{13}C $M(CO)_6$, employing acetone as an internal standard.[7]

Further studies of this unique reaction demonstrated the singular requirement to be the presence of at least one readily available coordination site for the (n-Bu)$_3$P=O, provided by a labile ligand. Thus analogous reactions with $py_3Mo(CO)_3$, $pyCr(CO)_5$, $pip_2W(CO)_4$, $pipW(CO)_5$, and $pipMo(CO)_5$ (py = pyridine and pip = piperidine) with ^{13}CO in the presence of excess (n-Bu)$_3$P=O all lead to $M(^{13}CO)_6$.[8] In the absence of the phosphine oxide, low levels of isotopic enrichment were obtained,[9] illustrating preferential replacement of the bound labile ligand by ^{13}CO as well as a profound difference in CO lability induced by the hard nitrogeneous bases compared with that of the phosphine oxide. Control experiments between $M(CO)_6$ and ^{13}CO in the presence of excess n-Bu_3P=O afforded *no* ^{13}C-enriched $M(CO)_6$ species. The skeletal sequence below summarizes these observations.



In a similar manner, although no enrichment of $Fe(CO)_5$ with ^{13}CO occurs in the dark with or without tri-n-butylphosphine oxide, the reaction of (py)$Fe(CO)_4$ with ^{13}CO in the presence of (n-Bu)$_3$P=O afforded the highly enriched $Fe(CO)_{5-n}(^{13}CO)_n$ species.[10,11] Other studies in progress in our laboratories involve assessing the generality of this process employing a wide variety of mononuclear and cluster metal carbonyl species, as well as the use of other highly directed oxygen bases.

The necessity of a labile ligand tends to suggest that the observed CO labilization by the phosphine oxide does *not* proceed by carbonyl carbon attack by the R_3P=O, the presumed pathway used by Me_3NO in its CO-labilizing activities.[12] If such were the case, ^{13}CO incorporation into $M(CO)_6$ (M = Cr, Mo, W) or $Fe(CO)_5$ should be as facile, if not more so, under the reaction conditions. In addition, GC analysis of the gases over the reaction showed no CO_2, a prominent product of the reactions in which $Me_3N \rightarrow O$ activates M-CO dissociation.[13] This might be anticipated, based on the much weaker N-O bond compared with the P-O bond. Our results indicate that the metal-bound phosphine oxide promotes CO loss and the initial tentative explanation is that the R_3PO ligand acts as a labilizing ligand relative to CO, of greater capabilities than pip or py.[14]

A recent report in the literature[15] of decarbonylation processes carried out under mild conditions can also be interpreted in terms of the CO-labilizing ability of phosphine oxide ligands, e.g., exhaustive decarbonylation of $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$, and $Ni(CO)_4$ was observed by hexamethylphosphoramide in the presence of the CO-abstracting reagent $[Rh(C_8H_{14})_2Cl]_2$ (C_8H_{14} = cyclooctene). The rhodium(I) abstraction of carbon monoxide may indeed be the homogeneous analogue to the palladium on charcoal carbonyl ex-

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