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.

References and Notes

(1) Harrick, N. J. "Internal Reflection Spectroscopy"; Interscience: New York, 1967; Chapter 7.
(2) Fahrenfort, J. *Spectrochim. Acta* **1961,** *17*, 698–709.
(3) Tompkins, H. G. *Appl. Spectrosc.* **1974,** *28*, 335–341.
(4) Blackwell, C. S.: Degen, P. J.; Osterholtz, F. D. *Appl. Spectrosc.* **1978,** *32*, 480–484.
(5) Palik, E. D.; Gilson, J. W.; Holm, R. T.; Hass, M.; Braunstein, M.; Garcia, B. *Appl. Optics*, **1978,** *17*, 1776–1785.
(6) Harrick, N. J. *J. Opt. Soc. Am.* **1965,** *55*, 851–857.
(7) Harrick, N. J.; Loeb, G. I. *Anal. Chem.* **1973,** *45*, 687–691.
(8) Ikeshoji, T.; Ono, Y.; Mizuno, T. *Appl. Optics* **1973,** *12*, 2236–2237.
(9) Gray, D. E., Ed. "American Institute of Physics Handbook", 3rd ed.; McGraw-Hill: New York, 1972; pp. 6–40 and 6–109.
(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 $\theta_c + 5.0°$ (θ_c = critical angle). The details will be published elsewhere in the near future.

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Received August 22, 1979

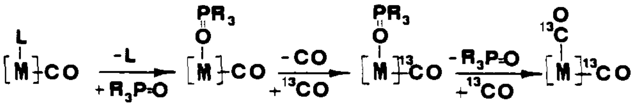
Synthesis of Metal Carbonyl Complexes Highly Enriched in Carbon-13: Utilization of the CO-Labilizing Ability of $(n\text{-Bu})_3P{=}O$

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 $(n\text{-Bu})_3P{=}O$ (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)$Cr[(n\text{-Bu})_3P{=}O](CO)_3$ 1981, 1917, and 1895 cm^{-1} and for $[(n\text{-Bu})_3P{=}O]_3Cr(CO)_3$ 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 $[(n\text{-Bu})_3P{=}O]_3Cr(^{13}CO)_3$ 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 $(n\text{-Bu})_3P{=}O$, 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 $(n\text{-Bu})_3P{=}O$ 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 $n\text{-Bu}_3P{=}O$ 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 $(n\text{-Bu})_3P{=}O$ 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 exchange process,[3] with both processes possibly proceeding via isocarbonyl intermediates or transition states (M—C≡O···Rh → M···C≡O—Rh → M···O≡C—Rh).[16] That is, the unsaturated metal carbonyl intermediate containing a binding site for the CO-labilizing $R_3P{=}O$ ligand in this instance is provided by rhodium(I) withdrawal of carbon monoxide with concomitant formation of $Rh(C_8H_{14})(CO)Cl$. It has not escaped our attention that the linear bridging carbonyl (η^2(C,O) CO) illustrated above, in addition to providing the first step in the CO abstraction process, also represents a highly directional oxygen donor which might itself promote lability in either of the metal centers.[16]

Acknowledgments. The financial support of the National Science Foundation through Grant CHE 78-01758 and of Tulane University is greatly appreciated.

References and Notes

(1) See, for example, Perutz, R.; Turner, J. J. *Inorg. Chem.* **1975,** *14*, 262.
(2) Darensbourg, D. J.; Murphy, M. A. *J. Am. Chem. Soc.* **1978,** *100*, 463.
(3) (a) Noack, K.; Ruch, M. *J. Organomet. Chem.* **1969,** *17*, 309. (b) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1977,** *99*, 7154.
(4) Darensbourg, D. J.; Salzer, A. *J. Am. Chem. Soc.* **1978,** *100*, 4119.
(5) The level of ^{13}CO enrichment was not extremely dependent on the quantity of excess $(n\text{-}Bu)_3P{=}O$ used, with phosphine oxide, metal ratios of 11:1 and 1.5:1 affording only slightly lower percentages of ^{13}CO in the $Cr(CO)_6$ products.
(6) Chandrasegaran, L.; Rodley, G. A. *Inorg. Chem.* **1965,** *4*, 1360.
(7) ^{13}C NMR spectra were determined at 15.03 MHz on samples of identical concentrations of natural-abundance and ^{13}CO-enriched $M(CO)_6$ species in acetone-d_6 solvent in 10-mm tubes employing a JEOL FX60 spectrometer. Spectra resulted from 1500–2500 transients with an acquisition time of 2.04, a pulse repetition rate of 5.0 s, and a flip angle of 30°. Quantitative intensity comparisons of the carbonyl resonances of acetone-d_6 at 205.1 ppm vs. that in the two samples were made to assess the level of ^{13}CO incorporation in the enriched sample. The agreement between ν(CO) infrared and ^{13}C NMR analyses was excellent.
(8) In a typical preparative-scale experiment, 0.47 g (1.00 mmol) of $py_3Mo(CO)_3$, 6.00 g (27.0 mmol) of $(n\text{-}Bu)_3P{=}O$, and 40 mL of dry hexane were placed in a 300-mL Schlenkware flask which was thoroughly degassed and refilled with 1.4 atm of ^{13}CO (~17.3 mmol). Heating at 70 °C with stirring for 16 h afforded upon workup $Mo(^{13}CO)_6$ in >50% purified yield. The workup procedure consisted of washing the hexane solution with two 80-mL portions of water to remove $(n\text{-}Bu)_3P{=}O$ and drying the hexane layer with $CaCl_2$, followed by vacuum distillation of the hexane solvent and sublimation of the hexacarbonyl product at 40 °C. Indications are that isolated yields may eventually be close to solution spectroscopic yields with improvements in techniques for separation of the volatiles, hexane and $Mo(^{13}CO)_6$.
(9) The level of ^{13}CO enrichment was observed to correspond to ^{13}CO replacement of the labile ligand (L) in the $L_nM(CO)_{6-n}$ starting materials, e.g., c-$Mo(CO)_4(pip)_2$ afforded $Mo(CO)_4(^{13}CO)_2$.
(10) Synthesis of $(py)Fe(CO)_4$ was accomplished using the procedure of Cotton and Troup.[11] The reaction of $(py)Fe(CO)_4$ with $(n\text{-}Bu)_3PO$ (1:2 molar ratio) was carried out in a ^{13}CO atmosphere at 50 °C in hexane solvent. After 4 h the level of ^{13}CO enrichment in the iron pentacarbonyl was ~70%.
(11) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974,** *96*, 3438.
(12) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975,** 829.
(13) CO_2 analysis was carried out on a Perkin-Elmer Sigma 2 gas chromatograph using a 6-ft, 0.025-in. stainless steel column packed with 80–100 mesh carbosphere (Alltech Associates) operated at 100 °C with helium as a carrier gas. The maximum level of CO_2 production would correspond to 0.003 mmol of CO_2/mmol of metal complex.
(14) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976,** *98*, 3160.
(15) Varshavsky, Yu. S.; Shestakova, E. P.; Kiseleva, N. V.; Cherkasova, T. G.; Buzina, N. A.; Bresler, L. S.; Kormer, V. A. *J. Organomet. Chem.* **1979,** *170*, 81.
(16) Indeed we have carried out preliminary experiments which indicate that $Rh(PPh_3)_2(CO)Cl$ activates CO displacement in reactions with $Cr(CO)_5(py)$, possibly resulting from initial Rh—C≡O···$Cr(CO)_5$ interaction.

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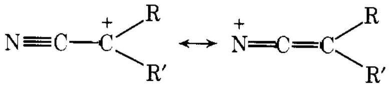
Received October 15, 1979

The α-Cyano Group as a Substituent in Solvolysis Reactions. An Evaluation of Inductive Destabilization vs. Mesomeric Stabilization of Cations by the Cyano Moiety

Sir:

Amazingly little is known about the effect of strong electron-withdrawing substituents on incipient carbonium-ion centers. Recently, interest in this area has been increasing.[1] We now report our preliminary results on the influence of the α-cyano group on incipient carbonium-ion centers and to propose that α-cyano groups are ambivalent in their relationships with attached carbonium-ion centers. Inductively, the cyano group is strongly destabilizing. However, much of this inductive effect can be balanced by a mesomeric (delocalization) effect involving resonance contributors **1** and **2**.



1 **2**

Interestingly, the resonance form **2** is a nitrenium ion, which should be much less stable than an analogous carbonium ion.[2] Thus, the extent to which **2** contributes to the structure of the intermediate cationic species will depend greatly on the nature of R and R′.[3]

Recently, Koshy and Tidwell have found that an α-trifluoromethyl group provides a rate retardation of 10^6 relative to hydrogen in the solvolysis of simple sulfonate esters.[1j] Similarly, Creary has found an H/α-keto rate ratio of 10^7.[1k] On the basis of the Taft polar substituent constants [$\sigma^*(NCCH_2)$ (1.30), $\sigma^*(CF_3CH_2)$ (0.92), and $\sigma^*(CH_3C({=}O)CH_2)$ (0.60)],[4] it might be predicted that an α-cyano moiety would have a greater rate retarding effect than either the α-trifluoromethyl or α-keto group. As shown in Table I, the influence of the α-cyano group on the rate of solvolysis of 2-propyl sulfonates resulted in an H/α-cyano (k_3/k_4) rate ratio of only 3.5×10^3. This is considerably smaller than the retardation factor expected on the basis of the Taft polar substituent constant and even less than the 10^4–10^7 rate retardation previously observed for β-cyano substitution.[11,5]

A number of different explanations might be suggested for the relatively small rate effect resulting from the introduction of the α-cyano group. Possibilities are (a) the reaction occurs by concerted elimination to give the only observed product methacrylonitrile; (b) the reaction occurs via solvent displacement followed by fast elimination of 2,2,2-trifluoroethanol; (c) the inductive destabilization of the cyano group is naturally less than calculated; or (d) the inductive destabilization of the cyano group is balanced by some other cation-stabilizing characteristic of the cyano group, namely mesomeric stabilization.

To evaluate the possibility of rate-limiting, concerted (E2) elimination, we measured the effect of β-deuterium substitution on the rate of solvolysis of 2-cyano-2-propyl trifluoromethanesulfonate. At 25 °C, a CH_3/CD_3 rate ratio[6] of 1.48 was observed. This value is very similar to the value of 1.46 found for 2-propyl p-bromobenzenesulfonate in trifluoroacetic acid.[7] More significantly, it is very close to the value of 1.54 obtained for the CD_3 isotope effect observed in the solvolysis of 2-trifluoromethyl-2-propyl p-toluenesulfonate.[1j] These values are too small for a rate-limiting, concerted elimination.[8,9] The observation of an isotope effect similar to that found in the presence of an α-trifluoromethyl group (which provides a 10^6 rate retardation) suggests that an α-cyano moiety should provide an even greater deceleration. However, this is not experimentally true.

Solvent participation in a S_N2 manner could be considered. 2,2,2-Trifluoroethanol is a relatively nonnucleophilic solvent which has been used widely for the study of solvolytic reactions because of this property. In addition, the isotope effect of 1.48 argues against such involvement.[9] To strengthen the basis for ruling out S_N2 involvement by solvent,[10] we solvolyzed the highly hindered 1-cyano-1-cyclooctyl tosylate (**7**) in 100% 2,2,2-trifluoroethanol. Cyclooctyl p-toluenesulfonate has been reported to solvolyze without nucleophilic solvent assistance

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