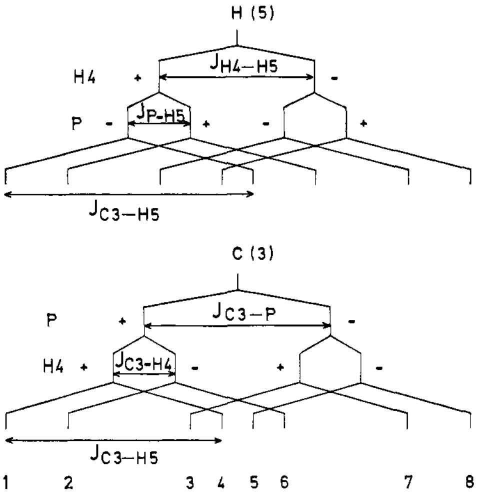

Figure 1. First-order stick diagrams of the H-5 proton (upper part) and C-3 carbon spectrum (lower part) in tri(3-bromo-2-thienyl)phosphine-*3*-^{13}C (see text). The relative magnitudes of the coupling constants are not drawn to scale.

$^2J_{CP}$ involving the non-proton-bonded C-3 atom in tri(3-bromo-2-thienyl)phosphine was attempted using $^{13}C-\{^1H\}$ double resonance techniques. It was found that the sign may be most conveniently obtained from the C-3 spectrum as observed under conditions of slight off-resonance irradiation of the H-5 inner satellites. However, this required a weaker decoupling field ($\gamma H_2/2\pi \approx$ 100–150 Hz) than that generally applied in off-resonance proton decoupling experiments. First-order stick diagrams showing the H-5 proton inner satellite spectrum and the undecoupled C-3 spectrum are presented in Figure 1. The spin states of the nuclei coupled to H-5 and C-3 are given for all transitions, with the convention that a positive sign for a low-field peak denotes a positive coupling to the nucleus in question. Magnitudes of the coupling constants were obtained from ^1H and undecoupled ^{13}C spectra (experimental parameters are given in the legend of Figure 2). The negative sign for J_{P-H-5} was determined from $^1H-\{^1H\}$ spin tickling experiments; otherwise the signs are indicated in accordance with literature data for related compounds and with the experiments described here.

The effect on the C-3 spectrum of irradiating in the proton region at a frequency slightly higher than any of the H-5 effective chemical shifts, $\nu_{H-5}^{eff} = \nu_{H-5} \pm {}^1/_2J_{H-5-H-4} \pm {}^1/_2J_{H-5-P}$, is shown in Figure 2 (actual values are given in the legend of Figure 2). Using the stick diagrams and signs indicated in Figure 1 it is estimated that under these experimental conditions the four reduced $J_{C-3-H-5}$ doublet splittings in the C-3 spectrum should show a wider spacing for the doublets in the order: [3–7] < [1–4] < [5–8] < [2–6]. As seen in Figure 2 the same order is followed for the reduced $J_{C-3-H-5}$ couplings in the experimental spectrum (the smallest reduced splitting observed in Figure 2 arises from $J_{C-3-H-5}$). Furthermore, the simulated double resonance spectrum obtained by diagonalization of the double resonance Hamiltonian matrix using the experimental parameters given in Figure 2 is shown below the experimental spectrum. The actual values for the observed (±0.03 Hz) and calculated (in parentheses) residual splittings are: [3–7] 0.45 Hz (0.44 Hz), [1–4] 0.60 Hz (0.59 Hz), [5–8] 0.62 Hz (0.60 Hz), and [2–6] 0.74 Hz (0.74 Hz). From the off-resonance decoupled spectrum the following sets of relative signs of coupling constants may be obtained: J_{C-3-P} and J_{H-5-P} are of opposite sign, *i.e.* $J_{C-3-P} > 0$; $J_{C-3-H-4}$ and $J_{H-4-H-5}$ have the same sign, *i.e.* $J_{C-3-H-4} > 0$.

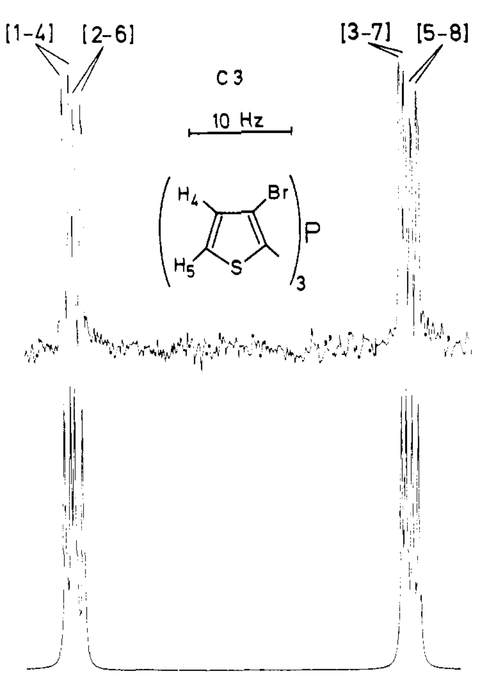

Figure 2. Experimental (upper part) and calculated (lower part) ^{13}C spectrum (55 scans) of C-3 in tri(3-bromo-2-thienyl)phosphine obtained during slight off-resonance (high-frequency) irradiation of H-5. The experimental parameters used for the simulation of the double resonance spectrum are: ν_2 = 756.30 Hz and $\gamma_{^1H}H_2/2\pi$ = 132.5 Hz for the irradiation frequency and amplitude, respectively; ν_{H-4} = 698.37 Hz, ν_{H-5} = 750.38 Hz, $J_{H-4-H-5}$ = +5.12 Hz, J_{P-H-4} = +2.45 Hz; J_{P-H-5} = −1.52 Hz, $J_{C-3-H-4}$ = +2.71 Hz, $J_{C-3-H-5}$ = +13.23 Hz, J_{C-3-P} = +32.90 Hz. The irradiation frequency and proton chemical shifts are relative to Me_4Si (100.1 MHz). ^{13}C nmr spectra were recorded on a Varian XL-100-15 spectrometer (25.2 MHz, ^2H lock, continuous wave mode, C-1024 CAT). The sample solution was *ca.* 38% w/w in CS_2-acetone-d_6 (50:12, w/w).

The off-resonance proton decoupling technique appears therefore to be generally applicable for determination of signs of ^{13}C–X coupling constants, *i.e.* it is not restricted only to carbon atoms which are directly bonded to protons.[5] Furthermore, under certain conditions it may also be useful for relative sign determination in cases where X = ^1H.

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CO_2 Fixation Leading to Stable Molecular Bicarbonato Complexes of d^8 Metals

Sir:

Although literally hundreds of carbonato–transition metal complexes are known,[1] isolable and well-defined analogous compounds containing *bicarbonate*

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(1) For a review, see K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 70, 171 (1970).

as a *ligand* appear to be at best scarce.[1,2] The aqueous solution chemistry of metal–bicarbonate systems, however, is rather extensive.[1] Particularly important—and pertinent to the present work—is the catalysis of carbon dioxide hydration by the enzyme (En) *carbonic anhydrase* which is postulated to involve reaction 1 as the first step (*cf.* eq 3),[3,4] and the recent work by Harris,

$$\mathrm{EnZnOH} + \mathrm{CO_2} \rightleftharpoons \mathrm{EnZnOCO_2H} \qquad (1)$$

et al., giving evidence for a similar reaction producing a short-lived cobalt–bicarbonato intermediate (eq 2).[5,6]

$$[(\mathrm{NH_3})_5\mathrm{Co(OH)}]^{2+} + \mathrm{CO_2} \rightleftharpoons [(\mathrm{NH_3})_5\mathrm{Co(OCO_2H)}]^{2+} \qquad (2)$$

We have synthesized thermally stable crystalline bicarbonato complexes of Ir(I) and Rh(I) through an analogous (eq 1 and 2) interaction between coordinated hydroxo group[7] and carbon dioxide (eq 3, M =

$$\underset{\mathrm{Ia,b}}{[(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{M(OH)}]} + \mathrm{CO_2} \xrightarrow{\mathrm{C_2H_5OH}} \underset{\mathbf{1a,b}}{[(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{M(OCO_2H)}]} \qquad (3)$$

Rh, Ir) in ethanolic solution suspension, followed by precipitation with hexane. The same bicarbonato species of rhodium (**1a**, see Scheme I) is obtained by simple metathesis involving bicarbonate ion and the labile perchlorato ligand[8] (eq 4) which lends support

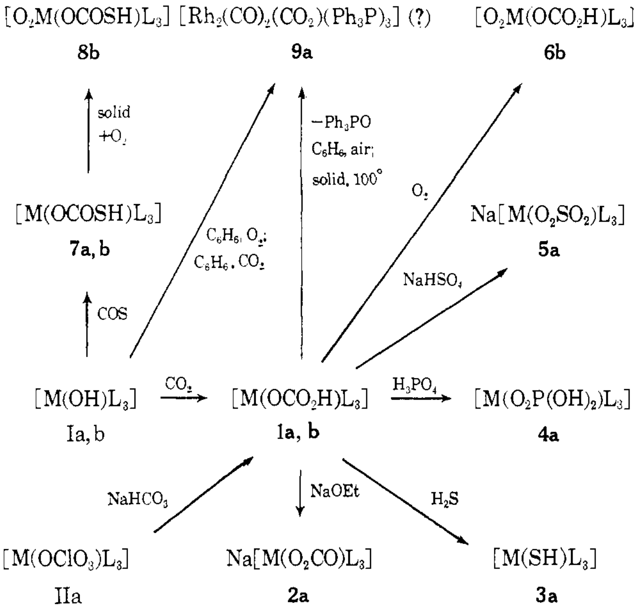
$$\underset{\mathrm{IIa}}{[(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{Rh(OClO_3)}]} + \mathrm{NaHCO_3} \xrightarrow{\mathrm{C_2H_5OH}} \underset{\mathbf{1a}}{[(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{Rh(OCO_2H)}]} + \mathrm{NaClO_4} \qquad (4)$$

for the CO_2 insertion reactions as formulated (eq 3).

The chemistry of the novel $MOCO_2H$ complexes and related compounds is summarized in Scheme I. Notable reactions include the preparation of the dihydrogen-phosphato (**4a**) and hydrogen-monothiocarbonato (**7a,b**) complexes and the formation of compound **9a** by diverse routes (**1a**, Ia → **9a**). This species (**9a**) appears to be identical (according to its ir spectrum) with the previously reported CO_2 complex, $[Rh_2(CO)_2(CO_2)(Ph_3P)_3]$,[9] and further characterization is in progress. The hydroxo complexes, $[M(OH)(CO)(Ph_3P)_2]$, react also with carbon disulfide, but no pure products have been obtained thus far.

Table I summarizes the infrared spectral data for the bicarbonato and related complexes. The carbonato species, $[Rh(O_2CO)(CO)(Ph_3P)_2]^-$ (**2a**), may contain bidentate O_2CO^{2-}.[10] There seem to be no precedents for the vibrational spectral analysis of coordinated bicarbonate and HCO_2S. The data for the OCO_2H complexes are sufficiently different from those of all known metal–CO_3 associations,[11] but in some respects similar to the spectra of bicarbonate ion.[10a,12] We tentatively consider that the present compounds involve a monodentate OCO_2H (*cf.* the constancy of the OCO_2H vibrations upon oxygenation of the Ir complex). The ν_{CO}'s of the metal-bonded carbonyls are in conformity with the usual experience with these types of Rh and Ir complexes,[7,8,13] and they thus corroborate the overall formulations.

Scheme I[a]



[a] $L_3 = (CO)(Ph_3P)_2$. M = Rh (**a**), Ir (**b**). Reaction medium is ethanol unless indicated otherwise. I,[7] II,[8] and **9a**[9] are previously reported compounds.

Table I. Principal Infrared Spectral Data (cm^{-1}) for Selected Complexes[a]

No.[b]	Complex[c]	ν_{CO} (metal)[d]	ν_{CO} (carboxylate)[e]
2a	$Na[Rh(O_2CO)(CO)L_2]$	1940	1620 s, 1350 m, 1053 m
1a	$[Rh(OCO_2H)(CO)L_2]$	1977	1655 s, 1368 s, 1290 s (br), 1083 m
1b	$[Ir(OCO_2H)(CO)L_2]$	1965	1655 s, 1368 s, 1285 s (br), 1088 m
6b	$[O_2Ir(OCO_2H)(CO)L_2]^f$	2016	1655 s, 1368 s, 1285 s (br), 1088 m
7a	$[Rh(OCOSH)(CO)L_2]$	1973	1626 s, 1169 w, 1159 w, 1115 s
7b	$[Ir(OCOSH)(CO)L_2]$	1959	1637 s, 1169 w, 1159 w, 1116 s

[a] Measured in Nujol. [b] See Scheme I. [c] L = Ph_3P. [d] All very strong. [e] Several lower frequency spectral bands have been omitted. [f] ν_{IrO_2}, 858 m.

There is one seemingly critical question concerning

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(2) Some evidence for a dimeric cobalt complex with coordinated bicarbonato groups has been recently reported by B. K. W. Baylis and J. C. Bailar, Jr., *Inorg. Chem.*, **9**, 641 (1970).

(3) M. E. Riepe and J. H. Wang, *J. Amer. Chem. Soc.*, **89**, 4229 (1967).

(4) (a) J. E. Coleman, *J. Biol. Chem.*, **242**, 5212 (1967); (b) J. E. Coleman, *Progr. Bioorg. Chem.*, **1**, 159 (1971).

(5) (a) E. Chaffee and G. M. Harris, Abstracts of Papers, 163rd National Meeting of the American Chemical Society, Boston, Mass., April, 1972, INOR 58; (b) E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, **95**, 4169 (1973); (c) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

(6) Metal–OCO_2H intermediates have been suggested also for related reactions, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 229 ff.

(7) L. Vaska and J. Peone, Jr., *J. Chem. Soc., Chem. Commun.*, 418 (1971).

(8) (a) J. Peone, Jr., and L. Vaska, *Angew. Chem., Int. Ed. Engl.*, **10**, 511 (1971); (b) L. Vaska and J. Peone, Jr., *Suom. Kemistilehti. B*, **44**, 317 (1971).

(9) Y. Iwashita and A. Hayata, *J. Amer. Chem. Soc.*, **91**, 2525 (1969).

(10) (a) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc., A*, 3137 (1958); (b) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayshi, *J. Amer. Chem. Soc.*, **79**, 4904 (1957).

(11) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 169 ff; (b) E. Kremer and C. R. Piriz Mac-Coll, *Inorg. Chem.*, **10**, 2182 (1971).

(12) (a) K. Nakamoto, Y. A. Sarma, and H. Ogishi, *J. Chem. Phys.*, **43**, 1177 (1965); (b) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(13) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968); *Inorg. Chim. Acta*, **5**, 295 (1971).

the bicarbonato complexes reported here; none of them show an O–H stretching frequency in their ir spectra, and the hydrogen is also not observable by the nmr. However, it is not unlikely that the unobservable proton is involved in intra- and/or intermolecular hydrogen bonding, and precedents of analogous cases are known.[14] The total properties of the key compound, $[Rh(OCO_2H)(CO)(Ph_3P)_2]$ (**1a**), leave little doubt about its formula: (1) complete elemental analysis; (2) nonelectrolyte in C_2H_5OH; (3) diamagnetism and electronic spectrum (λ_{max}, 355 nm), both are typical of Rh(I);[15] (4) formation, eq 3 *and* 4; and (5) expected reactions of a metal–OCO_2H group: (a) removal of the proton by base (**1a** → **2a**), and (b) addition of proton by acids, followed by replacement of H_2CO_3 (**1a** → **3a**, **4a**, **5a**).

The CO_2 fixation described here adds yet another mode of relatively few known carbon dioxide insertions into metal ligand or coordinated ligand bonds leading to isolable complexes: M–H, M–C, M–N, and MO_2[16] and $MOCH_3$.[17] In the present instance, the principal questions are (a) whether the bond rupture involves the M–O or O–H linkage and (b) whether the initial attack of CO_2 occurs on the metal center or the coordinated OH. The latter appears to be the case with *six*-coordinated cobalt(III) (d^6),[5] but here we deal with *four*-coordinated M(I) (d^8) complexes. It is hoped that planned mechanistic studies with labeled reactants will shed light on these problems.[18]

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(14) (a) Solid $KHCO_3$ shows a weak ν_{OH} band at 2620 cm^{-1}.[12a] (b) Internal hydrogen bonding has been observed between OCO_2 and H_3N in $[Co(OCO_2)(NH_3)_5]^+$, H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 3195 (1965). (c) See ref 2.

(15) J. Peone, Jr., Ph.D. Dissertation, Clarkson College of Technology, 1971.

(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1972, p 777 ff.

(17) T. Tsuda and T. Saegusa, *Inorg. Chem.*, **11**, 2561 (1972).

(18) We thank the National Institutes of Health and the Environmental Protection Agency for partial support of this research.

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Sulfurization as a Means for the Protection of Trivalent Phosphorus Atoms in the Syntheses of Methylated Poly(tertiary phosphines)

Sir.

Numerous poly(tertiary phosphines) with PCH_2CH_2P units have been synthesized by the base-catalyzed additions of phosphorus–hydrogen bonds to the vinyl double bonds in various vinylphosphine derivatives[1,2] such as diphenylvinylphosphine and phenyldivinylphosphine. However, up to the present time this preparative method has been limited to the syntheses of poly(tertiary phosphines) with phenyl groups bonded to the positions of the trivalent phosphorus atoms not occupied by the CH_2CH_2 bridges. Extension of this preparative method to the syntheses of poly(tertiary phosphines) with methyl groups, rather than phenyl groups, bonded to the free positions of the trivalent phosphorus atoms has been discouraged by the inconvenience of preparing and handling the very volatile and air-sensitive dimethylvinylphosphine and/or methyldivinylphosphine which would be required as starting materials. This communication reports a modification of this general preparative method which allows the syntheses of poly(tertiary phosphines) with $-CH_2CH_2P(CH_3)_2$ and $-CH_2CH_2P(CH_3)CH_2CH_2-$ units without the need to prepare and handle dimethylvinylphosphine and/or methyldivinylphosphine. The key feature of this new preparative method is the protection, as the corresponding phosphine sulfide, of the phosphorus atom(s) to which the methyl groups are bonded in the ultimate product. After the poly(tertiary phosphine) network is constructed by appropriate additions of phosphorus–hydrogen bonds to vinylphosphine sulfide derivatives, the protecting sulfur atom(s) are removed from the phosphine sulfide phosphorus atoms by treatment with lithium aluminum hydride in boiling dioxane to give the corresponding methylated poly(tertiary phosphine). The new methylated poly(tertiary phosphines) prepared by this method are of interest as potential ligands in coordination chemistry because they can act as multidentate ligands with very basic phosphorus donor atoms bearing methyl substituents. The partially sulfurized poly(tertiary phosphines) which are intermediates in this new synthetic method are also of interest in being readily accessible organophosphorus derivatives with phosphorus atoms in two different oxidation states.

An example of the application of this new preparative procedure is the synthesis of the di(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$, which is the first example of a potentially chelating di(tertiary phosphine) with aryl groups on one phosphorus atom and alkyl groups on the other phosphorus atom. Treatment of a tetrahydrofuran solution containing equimolar quantities of $(C_6H_5)_2PH$ and $(CH_3)_2P(S)CH{=}CH_2$ with a catalytic amount of potassium *tert*-butoxide gave, after an exothermic initial reaction and further heating at the boiling point for 26 hr, a 91% yield of the white crystalline diphosphine monosulfide $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$, mp 130.5°. Desulfurization of this product with excess $LiAlH_4$ in boiling dioxane gave an 80% yield of the liquid ditertiary phosphine $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$, bp 160° (0.05 mm). This product and the other new compounds described in this paper were identified by correct analyses for three elements and consistent proton and phosphorus-31 nmr spectra.

Similar synthetic methods can be used to prepare various tri(tertiary phosphines) of the type $R'P(CH_2CH_2PR_2)_2$ (I). Thus addition of $C_6H_5PH_2$ to 2 equiv of $(CH_3)_2P(S)CH{=}CH_2$ catalyzed by potassium *tert*-butoxide gave a 95% yield of the white crystalline triphosphine disulfide $C_6H_5P[CH_2CH_2P(S)(CH_3)_2]_2$, mp 162°, which underwent desulfurization with excess $LiAlH_4$ in boiling dioxane to give an 80% yield of the liquid tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$ (I: $R = CH_3$, $R' = C_6H_5$), bp 147° (0.08 mm). Base-catalyzed addition of 2 equiv of $(C_6H_5)_2PH$ to $CH_3P(S)(CH{=}CH_2)_2$ gave a 95% yield of the white crystalline triphosphine monosulfide $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$, mp 130–131°, which underwent desulfurization with $LiAlH_4$ in boiling dioxane to give a 57% yield of the white crystalline tri(tertiary phosphine) $CH_3P[CH_2$-

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(2) R. B. King, *Accounts Chem. Res.*, **5**, 177 (1972).