dence that the phosphine forms an adduct first is observed in the nmr spectrum (Figure 1) where the "triplet" centered near τ 7.8 arises from the previously described pattern arising from Pt–H and P–H coupling.

The geometry of the five-coordinate phosphine adduct of II cannot be unequivocally determined from the nmr data, but certain limitations are placed on this geometry by the observation of sharp, unsplit ethyl resonances. (1) The complex may be square pyramidal with symmetry equivalent ethyl groups and a lifetime long on the nmr time scale. (2) The complex may be either square pyramidal or essentially trigonal bipyramidal with rapid rotation about the S_2C–N bond equilibrating the ethyl groups. (3) The ground-state geometry may be trigonal bipyramidal with a lifetime short on the nmr time scale. Further studies are necessary to distinguish between these possibilities.[7]

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Sulfur Dioxide Insertion. V. A New Mode of Addition of Sulfur Dioxide to a Metal–Carbon Bond[1]

Sir:

The reactions between sulfur dioxide and complexes containing transition metal–carbon σ bonds have invariably afforded addition products with a sulfone ($M-SO_2-C$) type linkage (S-sulfinates).[2,3] In the case of σ-allyl (2-alkenyl) complexes, rearrangement of the hydrocarbon moiety frequently accompanies such insertion.[1,4]

This latter observation prompted us to investigate reactions between sulfur dioxide and 2-alkynylmetal compounds in order to ascertain whether the insertion occurs with rearrangement to the 1,2-alkadienylsulfinato derivatives (1).

$$M-CH_2-C\equiv C-R + SO_2 \longrightarrow M-SO_2-C(R)=C=CH_2 \quad (1)$$

The complex $Mn(CO)_5CH_2C\equiv CH$ (**1**) was synthesized by a slow addition of $NaMn(CO)_5$ (prepared from 2.0 g of $Mn_2(CO)_{10}$ and excess sodium amalgam[5]) to 1.54 g (0.013 mole) of propargyl bromide in tetrahydrofuran at 0° followed by vigorous stirring for 1.5 hr. The solution was then filtered through Zeolite, the solvent was removed *in vacuo* at 0°, and the residue was sublimed at 25° (~0.1 mm) onto a probe cooled to −78°. The yield of a light yellow solid was 2.26 g (90%). *Anal.* Calcd for $C_8H_3O_5Mn$: Mn, 23.5. Found: Mn, 23.4. The product is extremely temperature sensitive, decomposing rapidly at 25°. However, it can be stored indefinitely at −78° and appears to be unaffected by air.

The infrared spectrum of **1** in the carbonyl stretching region consists of the absorption bands assigned as follows: 2118 (w), A_1 (CO); 2099 (vw), $C\equiv C$;[6] 2056 (w), B (CO); 2022 (vs), E (CO); 1990 (s), A_1 (CO); and 1975 cm^{-1} (vw), ^{13}CO (cyclohexane solution). The proton magnetic resonance spectrum exhibits a doublet at τ 8.64 and a 1:2:1 triplet at τ 7.79 ($J \sim 3$ cps), the relative intensities being 2:1, consistent with the presence of the 2-propynylmanganese moiety ($MnCH_2C\equiv CH$). To our knowledge, this compound represents the first authentic 2-alkynyl derivative of a transition metal.[7-9]

The interaction of 2-propynylmanganese pentacarbonyl with SO_2 in pentane at 25° leads to a rapid deposition of a light yellow solid. The reaction is complete within 15 min, affording a nearly quantitative yield of the product. After removal of the solvent, the residue crystallizes from chloroform–pentane. Additional purification may be effected by sublimation at 75° (~0.1 mm) to produce white needles (**2**), mp *ca.* 112° (dec). *Anal.* Calcd for $C_8H_3O_7SMn$: C, 32.25; H, 1.15; S, 10.74; mol wt, 298. Found: C, 32.42; H, 1.18; S, 10.56; mol wt (osmometry in $CHCl_3$), 304, 295, 289. A virtually quantitative yield of the compound has been also obtained from $Mn(CO)_5CH_2C\equiv CH$ and liquid SO_2 at −70°.

The structure of the product may be arrived at with the aid of infrared and proton magnetic resonance spectroscopy. The carbonyl stretching frequency region of the infrared spectrum consists of absorptions at 2128 (m), 2068 (w), 2035 (vs), and 2010 cm^{-1} (s) (CCl_4 solution). The relative positions and intensities of these bands are similar to those found for a number of $Mn(CO)_5(SO_2R)$ complexes[1,2,10,11] and support the presence of a pentacarbonyl moiety in conjunction with an Mn–S bond. In the 1300–800-cm^{-1} region prominent absorptions are present at 1110 (s), 993 (w), 906 (s), and 808 cm^{-1} (m–s) (KBr pellet). The absence of sulfur–oxygen stretching frequencies in the regions 1220–1185 and 1090–1040 cm^{-1} contrasts the spectral behavior of $Mn(CO)_5(SO_2R)$ and militates against an $Mn-S(O)_2-C_3H_3$ structural assignment. However, the absorptions at 1110 and either 906 or 808 cm^{-1} may be attributed to the SO stretching frequencies in an $Mn-S(O)-O-C_3H_3$ linkage.[12,13]

The nmr spectrum of **2** (Figure 1) shows a 1:2:1 triplet at τ 3.52 ($J \sim 2.5$ cps) and a quartet in the region τ 4.28–5.03, each component of which is split into a doublet (separation ~2.5 cps). The intensities of the triplet and the two quartets are in the ratio 1:2. The complete absorption pattern is characteristic of an ABX spectrum with $J_{AX} = J_{BX}$[14] and upon analysis yields τ 4.47 and 4.84 for protons A and B and $J_{AB} \sim 15$ cps.

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[1] For part IV of this series, see F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Am. Chem. Soc.*, **89**, 2493 (1967).

[2] F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966).

[3] J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966).

[4] A. Wojcicki, R. L. Downs, and F. A. Hartman, Abstracts of the 3rd International Symposium on Organometallic Chemistry, Munich, Germany, 1967, p 320.

[5] R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 198 (1963).

[6] The band was assigned on the basis of its position and relative intensity; see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 59–61.

[7] The complex $C_5H_5Fe(CO)_2CH_2C\equiv CH$, reported by Ariyaratne and Green,[8] gives the nmr spectrum showing equivalence of the three C_3H_3 protons and most likely should be reformulated as $C_5H_5Fe(CO)_2$-$C\equiv CCH_3$.[9]

[8] J. K. P. Ariyaratne and M. L. H. Green, *J. Organometal. Chem.* (Amsterdam), **1**, 90 (1963).

[9] R. L. Downs, private communication, The Ohio State University, 1967.

[10] F. A. Hartman, Ph.D. Thesis, The Ohio State University, 1966.

[11] E. Lindner and H. Weber, *Angew. Chem.*, **78**, 752 (1966).

[12] S. Detoni and D. Hadži, *J. Chem. Soc.*, 3163 (1955).

[13] S. Braverman and H. Mechoulam, *Israel J. Chem.*, **5**, 71 (1967).

[14] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 89–91.

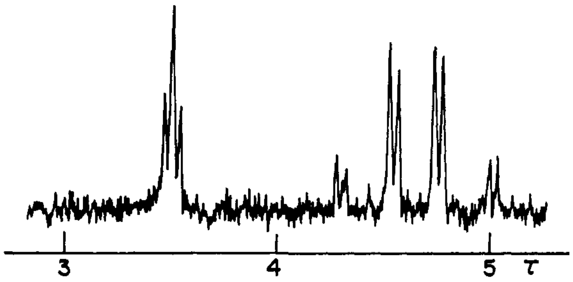
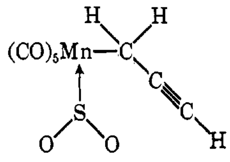


Figure 1. Proton magnetic resonance spectrum of $Mn(CO)_5SO_2$-C_3H_3 (recorded on a Varian Associates A-60 spectrometer in $CDCl_3$ solution).

The chemical shift of the unique proton (X) precludes retention of the $-CH_2C{\equiv}CH$ structure by the C_3H_3 fragment upon insertion but is compatible with either an SCH= or an OCH= linkage.[13,15] The hydrogens A and B absorb in the region assigned to olefinic or allenic protons,[15] and their nonequivalence may be due to the presence of the asymmetric sulfur in the compound.[16]

The proposed $(CO)_5MnS(O)OCH{=}C{=}CH_2$ structure is consistent with the absence of a C≡C stretching frequency in the infrared spectrum of **2**; interestingly, however, there is no absorption which could be assigned to a carbon–carbon stretching frequency of an allenic moiety. Nevertheless, it appears reasonable that such a band may be hidden underneath a very intense carbonyl stretching absorption at 2010 cm^{-1}.

The formation of $(CO)_5MnS(O)OCH{=}C{=}CH_2$ rather than the corresponding sulfinate may be rationalized in terms of the geometry of the parent 2-propynyl complex and a relatively facile 2-alkynyl to 1,2-alkadiene rearrangement. Assuming that the SO_2 sulfur interacts with manganese in the initial step of the insertion, the C(3) atom of C_3H_3 is placed in an unfavorable position for migration onto that sulfur because of the linearity of the C—C≡CH moiety (I). By way of contrast, the SO_2 oxygens are in a close proximity to the C(3) atom and can accept the migrating C_3H_3 fragment. The alternative route—direct insertion of SO_2 into the Mn–CH_2 bond—is apparently energetically less favorable than the concerted process leading to rearrangement.



I

Finally, two remarks are in order. First, the course of this insertion indicates that sulfur dioxide may function as an electrophilic rather than a nucleophilic reagent toward the metal,[17] assuming, of course, that the mechanism proposed above is operative. Second, the formation of a complex containing an S–O–C linkage demonstrates that such derivatives may, with certain systems, be the kinetically favored products which once formed exhibit a high degree of thermodynamic stability. Indeed, all attempts at isomerization of $(CO)_5MnS(O)OCH{=}C{=}CH_2$ to the corresponding S-sulfinate by heating it in chlorobenzene, benzene, tetrahydrofuran, and chloroform proved unsuccessful.

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[15] L. M. Jackman, ref 14, pp 60–62.

[16] Although, to our knowledge, organic allenes with such asymmetry have not been investigated, there are numerous examples of magnetic nonequivalence of methylene protons adjacent to an asymmetric center; see L. M. Jackman, ref 14, pp 99–103.

[17] Electrophilic attack of SO_2 on $C_5H_5Rh(C_2H_4)_2$ to give C_5H_5Rh-$(C_2H_4)(SO_2)$ has been recently suggested by Cramer.[18]

[18] R. Cramer, *J. Am. Chem. Soc.*, **89**, 5377 (1967).

Radical Transfer in a CIDNP Raser

Sir:

Ward and Lawler recently predicted[1] that pmr emission should be observed for products, in addition to the alkenes, which are formed from radical intermediates of alkyllithium–bromoalkane reactions. This radiofrequency amplification by stimulated emission of radiation (raser) produced by chemically induced dynamic nuclear polarization (CIDNP) was confirmed in their subsequent report.[2] They reported CH_2 emission for ethylbenzene formed by treating 2-bromoethylbenzene and *t*-butyllithium. However, each of the products observed to date as an emitter has as a structural component one of the initially generated radicals. Therefore, I wish to report raser action in a compound formed by radical transfer.

The system which gave a radical-transfer product was comparable to that previously reported.[1] However, a change in the Lewis base, employed to depolymerize the alkyllithium hexamer with concomitant enhancement of the radical-generation reaction, gave additional negative pmr peaks. Figure 1 shows the pmr spectra, measured on a Varian A-60A spectrometer, for the system *n*-butyllithium in hexane (0.6 ml of 1.5 *M*, Foote Mineral Co.), 1-bromobutane (60 μl), and anhydrous triethylamine (0.25 ml).[3] Although the order of mixing these components was unimportant, in the example 1-bromobutane was added to the *n*-butyllithium solution (Figure 1.1) to give a mixture of the radical generation reagents (Figure 1.2). The triethylamine was then rapidly added, and repeated scans were run over the pmr region from δ 6.5 to 3.0 ppm.[4] The series of absorption and emission bands (Figure 1.3)[5] built up in 2–3 min and then slowly decreased, giving the weak absorption spectrum in Figure 1.4 after 10 min.

[1] H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

[2] *Chem. Eng. News*, 46, 40 (Jan 15, 1968).

[3] Considerable variation in the quantities of 1-bromobutane and triethylamine showed qualitative concentration effects including the loss of raser action where the reaction rate was very slow. High concentrations led to uncontrollably fast reactions or reactions which were complete in less than the pmr scan times.

[4] Other regions of the spectrum were searched, including the $-CH_2Li$ range, δ 0 to −2, but no additional emission bands were detected. The regions 0.7–1.9 and 2.3–2.7 were not accessible because of solvent and triethylamine ($-CH_2N$) absorption, respectively. TMS was used as an internal calibration standard in most experiments.

[5] Scan time for this sweep was approximately 2 min and was started at 0.8 min after mixing of triethylamine.