Table I. ^1H and ^{13}C NMR Parameters of **5**[a]

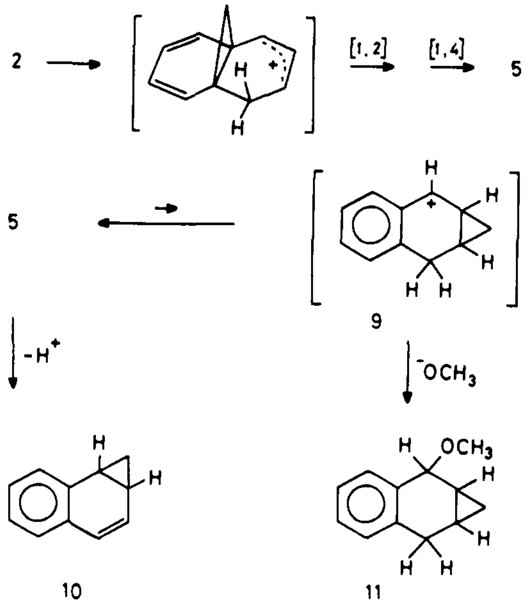
position	$\delta_{^1H}$	$\delta_{^{13}C}$
1	4.0 (m)	43.7 (d, 177)
2a	2.55 (d, t; ≈10, 2)	63.5 (t, 172 ± 2)
2b	4.50 (t, m; ≈8, 2)	
3	4.0 (m)	51.7 (d, 191.6)
4	10.38 (d, 7)	221.2 (d, 168.0)
5	4.0 (m)	31.3 (t, 132.4)
6		146.3 (s)
7	7.77 (d, 7)	132.2 (d, 166.3)
8	8.23 (t, d; 7, 1.5)	146.8 (d, 165.4)
9	7.82 (t, 7)	130.8 (d, 169.0)
10	8.11 (d, 7)	140.1 (d, 169.0)
11		133.8 (s)

[a] ^1H and ^{13}C chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (J_{HH} and $^1J_{CH}$ in hertz) are in parenthesis.

5 in sodium bicarbonate buffered methanol at −78 °C afforded **10** (13%) and **11** (87%).[8] This may be explained by assuming an equilibrium between ion **5** and the ^1H NMR undetected ion **9**[9] (thus present for at most 5%), which is therefore very far to the side of **5**, vide infra. Because of the low basicity of the methoxide, the proton abstraction from **5**, yielding **10**, will be slow, whereas the nucleophilic attack on **9**, resulting in the formation of **11**, is considered to be rapid (see Scheme I).

A close examination of the NMR characteristics of the aliphatic signals of **5**, of which the cyclopropylcarbinyl cationic moiety (**6**) has a fixed geometry, reveals the following for this structural element. Firstly, the H(4) resonance shows a vicinal coupling with H(3) ($J = 7$ Hz), but not with the H(5) hydrogens ($J < 1$ Hz). This may be interpreted in terms of a more or less flat "naphthalenium" skeleton; i.e. C(5), C(4)H, C(3), and C(1) are in one plane. Secondly, C(2) is deshielded relative to both C(1) and C(3), and H(2b) is deshielded relative to both H(1) and H(3); therefore it can be argued that position 2 carries some positive charge. [H(2a) is observed at high field (δ 2.04) because of shielding by the benzene ring]. Thirdly, the smaller $^1J_{CH}$ value of C(2) H_2 (172 ± 2 Hz) compared with C(1) H (177 Hz) and the large value of 191 Hz for C(3) H indicates both some weakening of the C(2)-C(3) bond and some double-bond character of the C(3)-C(4) linkage. Finally, it is of interest to note that H(2a) has a vicinal coupling with H(1) of ~10 Hz and with H(3) of ~2 Hz, whereas H(2b) has a vicinal coupling with both H(1) and H(3) of 7-8 Hz [the geminal coupling constant for C(2) H_2 is only ~2 Hz]; these phenomena indicate an increase of the H(1)-C(1)-C(2)-H(2a) dihedral angle, and are also in line with the suggested partial positive charge at C(2) and the coupled weakening of the C(2)-C(3) bond.

Scheme I



The proposed geometry of the moiety **6** in ion **5** compares with the conformation of the cyclopropylcarbinyl cation ($C_4H_7^+$), which was recently calculated to be only 0.5 kcal mol^{-1} higher in energy than the (most stable) bisected form.[10]

Further and more detailed work on the cyclopropylcarbinyl cation moieties present in ions resulting from protonated annulenes is currently in progress.

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(8) The assignments were based on ^1H and ^{13}C NMR data and an exact mass determination of the mixture of the products.
(9) Because of the large amount of **11** obtained after quenching, it might be argued that the ion observed by NMR is actually **9** instead of **5.** Such a view is, however, ruled out on the basis of (i) the NMR data (Table I) and (ii) a comparison of these data with those of the homologous ions obtained from the methyl substituted 1,6-methano[10]annulenes (see note 5). For example, 2-Me-**2** rearranges to 1-Me-**5** and not to Me-**9**, as was concluded from, e.g., the presence of the ^1H NMR doublet at δ 9.98, assigned to H(4).
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Formation of Methane and Ethane by Reduction of Carbon Monoxide Coordinated through Both Carbon and Oxygen on $Mg[CpFe(CO)_2]_2 \cdot 4THF$

Sir:

Facile catalytic hydrogenation of carbon monoxide would supply a very important step in the conversion of coal into other fuel sources. Considerable interest and activity in the homogeneous reduction of CO has been shown in recent years, although catalytic systems have been elusive. In our examination of reactions of carbon- and oxygen-coordinated CO, we have found that the CO coordinated in this manner can be reduced to mixtures of methane and ethane under mild conditions on the complex $Mg[CpFe(CO)_2]_2 \cdot 4THF$.

Homogeneous reductions of carbon monoxide to methane,[1-3] mixtures of alkanes,[4,5] methanol,[6] and a mixture of linear alcohols[7] have been observed. Only in Bercaw's zirconium system is there an understanding of the steps of the

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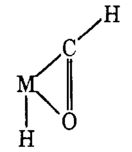
reaction,[6,8-10] although recent work by Casey et al.,[11] Gladysz et al.,[12] and Graham et al.[13] on reactions of Re-formyl species may be useful in interpreting CO reduction reactions. Several of the observed homogeneous reductions of CO involve aluminum compounds,[4,5,7] which are known to readily coordinate to the oxygen of a bound CO (A).[14,15] In other cases of CO reduction, it has been suggested that intermediates with side-bonding CO may be involved (B).[2,6] To examine the importance of coordination of both carbon and oxygen for reduction of CO, we have begun a study of reactions of complexes with this dual coordination.

$$M—C{=}O—AlR_3$$

A



B

The complex $Mg[CpFe(CO)_2]_2{\cdot}4THF$ was prepared by reacting a twofold excess of Mg amalgam (Mg chips + $HgCl_2$ in THF) with $[CpFe(CO)_2]_2$ in THF for 2 h at room temperature. Filtration produced a rust-colored solution from which rust-colored crystals of $Mg[CpFe(CO)_2]_2{\cdot}4THF$ could be precipitated by addition of hexane. The infrared spectrum in THF [2010 (w), 1948 (w), 1916 (s), 1883 (vs), 1852 (s), and 1712 (vs) cm^{-1}] was in good agreement with that previously reported.[16]

The lithium complex, $LiCpFe(CO)_2$, was prepared by reacting $[CpFe(CO)_2]_2$ with a 10-fold excess of Li in THF for 4 h. The infrared spectrum [1884 (s), 1869 (s), 1812 (s), 1788 (w), and 1750 (s) cm^{-1}] was as expected.[17]

The Mg complex exists in solution as a dynamic equilibrium between the bis- and tetrakis-THF adducts:

$$Mg[CpFe(CO)_2]_2{\cdot}2THF + 2THF \rightleftarrows Mg[CpFe(CO)_2]_2{\cdot}4THF$$

The bis-THF complex shows two strong carbonyl absorptions in the infrared at 1920 and 1850 cm^{-1}, intermediate in frequency between those in the covalent mercury complex, $Hg[CpFe(CO)_2]_2$, and the anion, $CpFe(CO)_2^-$, and can be assigned to a metal-metal bonded species, Fe—Mg—Fe.[17] The tetrakis-THF adduct exhibits two strong infrared absorptions at 1884 and 1713 cm^{-1}. The low-frequency band, which is 60 cm^{-1} lower in frequency than the absorptions in $CpFe(CO)_2^-$, is almost certainly the result of a carbon- and oxygen-coordinated species, Mg—O═C—Fe, with a structure similar to that of $Mg[CpMo(CO)_3]_2{\cdot}4py$.[18]

Treatment of $Mg[CpFe(CO)_2]_2{\cdot}4THF$ with a 30-fold excess HCl in THF at −198 °C and allowing the solution to warm to room temperature resulted in the formation of methane, ethylene, and ethane in the ratio 1:0.3:0.7 as shown by gas chromatographic analysis on Spherocarb and Poropak Q columns. The reaction is complete in 10 h at room temperature. The total yield of hydrocarbons is 5%. The solution remains homogeneous throughout the reaction with $HFe(Cp)(CO)_2$ the only CO-containing product at the end of the reaction.[19] Use of DCl leads to CD_4 and a trace of CD_3H (the amount of CD_3H is 5% of that of CD_4). Equal amounts of C_2D_6 and C_2D_5H are also observed by GC-MS. The deuterium incorporation into ethylene could not be evaluated because of the relatively small amount of ethylene in the sample. C-13-enriched (75%) $Mg[CpFe(CO)_2]_2{\cdot}4THF$ was prepared from the enriched dimer $[CpFe(CO)_2]_2$.[21] Reaction of this species with DCl led to $^{13}CD_4$ and $^{13}C_2D_6$ confirming that CO reduction has been effected.

The lithium complex, $LiCpFe(CO)_2$, also exhibits an oxygen-bonded CO in THF as shown by the strong infrared absorbance at 1750 cm^{-1}.[22] When this complex is treated with excess HCl under similar conditions, CH_4, C_2H_4, and C_2H_6 are formed (1:0.4:1) with a total yield of 10%. When it is treated with DCl, CD_4, C_2D_6, and C_2D_5H are formed, behavior very similar to that of the Mg complex.

The source of ethylene is uncertain. Labeling studies have not been successful because of the low yield. While it is likely that ethylene is formed as a result of the reduction of CO, possibly as an intermediate in the formation of ethane, the possibility of its being formed by decomposition of THF cannot be ruled out. $Mg[CpFe(CO)_2]_2{\cdot}2THF$ reacts with HCl in toluene solution forming amounts of methane and ethane comparable with those observed in THF while the quantity of ethylene is reduced by a factor of 10. For the Li compound, reaction with HCl in toluene produces no ethylene and the quantities of methane and ethane are not significantly reduced.

The reduction of CO on $Mg[CpFe(CO)_2]_2{\cdot}2THF$ in toluene solution is interesting because the predominant species present is the Mg—Fe bonded species. We believe that, under the reaction conditions (i.e., presence of HCl), the equilibrium is shifted toward the oxygen-coordinated form and then reduction of the CO occurs. $Hg[CpFe(CO)_2]_2$, which has a Hg—Fe bond and no capability for oxygen coordination, produces no hydrocarbons when treated with HCl under identical conditions with those used for the Mg and Li complexes. At the other extreme, $NaFe(Cp)(CO)_2$, which has a weak interaction to the oxygen, shows smaller amounts of methane and ethane under similar conditions.

The reduction of CO on $Mg[CpFe(CO)_2]_2{\cdot}4THF$ occurs at −78 °C, although at a slower rate. The product distribution was unaltered. The presence of H_2 has no effect on the reduction; $Mg[CpFe(CO)_2]_2{\cdot}4THF$ reacts with HCl and D_2 with no deuterium incorporation into the hydrocarbons. The absence of light showed no difference in quantity or distribution of products.

The formation of hydrocarbons occurring at −78 °C and formation of some CD_3H and C_2D_5H when DCl was used suggests formation of a very reactive intermediate. We believe the most likely intermediate is $[Cp(CO)(THF)Fe{=}CH_2]^+$ which has precedent in the work of Brookhart.[23-25] Similar iron carbenes are strong hydrogen abstractors, and could react with solvent to form $FeCD_2H$, with DCl to form $FeCD_3$, or with FeMe to form ethane derivatives. We have observed that $CH_3Fe(Cp)(CO)_2$ reacts quite readily with HCl generating CH_4 and $HFe(Cp)(CO)_2$[26] which are two of the observed products of the CO reduction reaction. Experiments are in progress to ascertain whether the carbene is indeed an intermediate.

Although our present data are insufficient to postulate a mechanism for these reactions, the methane and the ethane are formed as the result of reduction of coordinated CO and may involve Fischer-Tropsch-type reactions. The importance of coordination of CO through both carbon and oxygen for reduction has been previously suggested and our present results give support to this proposal.[5] We are in the process of attempting to elucidate mechanistic information by variable-temperature NMR and of investigating the reactivity of other complexes that have carbon monoxide coordinated through carbon and oxygen.

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(19) The observation of $HFeCp(CO)_2$ is somewhat surprising since this complex readily decomposes to $[CpFe(CO)_2]_2$. Evidently the hydride is stabilized under the reaction conditions.

(20) GC–MS work was done at the Mass Spectral Facility, Cornell University.

(21) $[CpFe(CO)_2]_2$ was enriched to 75% as determined by infrared spectroscopy by treatment of a toluene solution at 80 °C with two successive portions of 99% ^{13}CO.

(22) Three species exist in THF solution, $(Cp)(CO)_2Fe–Li$ (I), $[(Cp)(CO)_2Fe^-](Li^+)$ (II), and $Cp(CO)Fe–CO–Li$ (III), with ~60% III being present.[16]

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(26) The chloride, $CpFe(CO)_2Cl$, is also formed.

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Oxygen Chiral Phosphodiesters. 1. Synthesis and Configurational Analysis of Cyclic [^{18}O]-2′-Deoxyadenosine 3′,5′-Monophosphate

Sir:

It is now generally accepted that stereochemical investigation of the mechanism of a phosphotransferase reaction is the most direct method for determining whether the mechanism involves the formation of a covalent adduct between the enzyme and substrate. The majority of these experiments have been carried out with phosphorothioate mono- and diesters. The use of sulfur analogues of the normal substrates simplifies the synthesis and configurational analysis of the chiral substrate and product, but the presence of sulfur often decreases the velocity of the enzymic reaction and may introduce some uncertainty in interpretation of results when coordination of the substrate by a metal ion is required for catalysis.[1] Phosphate esters which are chiral by virtue of oxygen isotopes cannot pose such problems. Knowles' group recently reported the syntheses of a number of $^{16}O,^{17}O,^{18}O$-labeled chiral phosphate monoesters and described an elegant mass spectral technique for the configurational analysis of such esters.[2] These esters have been used to probe the mechanisms of a number of enzyme-catalyzed reactions, including demonstration of a retention of configuration at phosphorus during the reaction catalyzed by the alkaline phosphatase from *Escherichia coli*[3] and an inversion of configuration in the reaction catalyzed by glycerol kinase.[4] However, many phosphotransferases catalyze reactions involving phosphate diesters, and Knowles' synthetic method is not amenable to their preparation. In this communication we report the stereospecific synthesis of both diastereomers of cyclic [^{18}O]-2′-deoxy-AMP and a simple method for the direct determination of their absolute configurations at phosphorus.

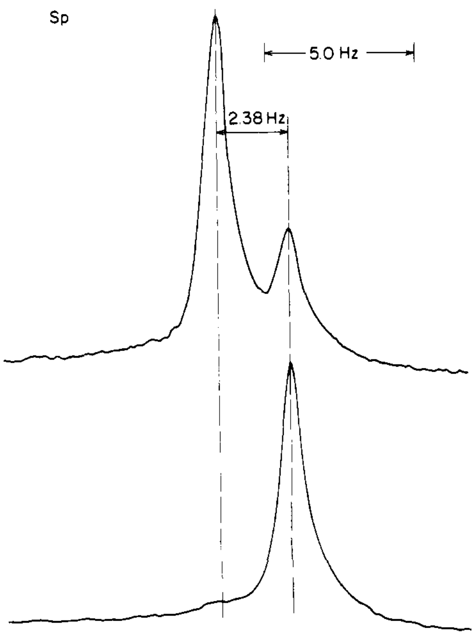

Figure 1. 80.9-MHz ^{31}P NMR spectra of cyclic [^{18}O]-2′-deoxy-AMP prepared from the axial *P*-anilidate diluted (top) and undiluted (bottom) with unlabeled cyclic 2′-deoxy-AMP. The samples were prepared in 0.10 M EDTA, pH 7.0, containing 20% D_2O. The approximate chemical shift of the unlabeled cyclic 2′-deoxy-AMP is 2.6 ppm (upfield shift relative to an external capillary containing 85% H_3PO_4). The total concentration of cyclic 2′-deoxy-AMP is 20 mM in each sample.

The diastereomeric *P*-anilidates of cyclic 2′-deoxy-AMP can be readily prepared by the stereospecific potassium *tert*-butoxide catalyzed cyclization of diastereomerically pure samples of 2′-deoxy-3′-(*o*-chlorophenyl-*N*-phenyl phosphoramidate)adenosine.[5,6] Stec's group has demonstrated that *P*-anilidates react smoothly with carbon disulfide after treatment with sodium hydride to provide the corresponding phosphorothioates.[7] This reaction was found to proceed with retention of configuration at phosphorus, as would be predicted on the basis of apical attack–apical departure from a pentacoordinate intermediate. We have found that the sodium salts of *P*-anilidates also react smoothly with carbon dioxide in pyridine to provide the phosphate diesters in quantitative yield.

When the *P*-anilidates of cyclic 2′-deoxy-AMP were reacted separately with a tenfold excess of 99% enriched $C^{18}O_2$ and the products purified by chromatography on DEAE-Sephadex A-25,[8] phosphodiesters were obtained which were identical with authentic cyclic 2′-deoxy-AMP using the criteria of TLC, ^1H NMR at 270 MHz, and ^{31}P NMR at 32 MHz. The presence of ^{18}O in the diesters was confirmed by examination of ^{31}P spectra which were obtained at 80.9 MHz using a 250-Hz sweep width, 16K data points (0.03 Hz/real data point), and 40 transients. In Figures 1 and 2 we present these spectra and those obtained under identical conditions when the two labeled diesters were mixed with a threefold molar excess of unlabeled cyclic 2′-deoxy-AMP. In the spectra recorded on the undiluted samples, one major resonance and one minor resonance are observed. In the spectra recorded on the isotopically diluted samples, the same two resonances are observed, with the upfield resonance being associated with the labeled diester.[9] The minor resonance in the spectra of the undiluted samples is due to a small amount of unlabeled cyclic 2′-deoxy-AMP. The ^{18}O perturbation in the diester prepared from the axial anilidate is 2.38 Hz, and that in the diester prepared from the equatorial anilidate is 2.56 Hz. A spectrum was obtained at 145.7 MHz on a sample containing 12 mM unlabeled cyclic 2′-deoxy-AMP

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