palladium chloride complexes with a variety of nucleophiles have been reported.[2] However, the cyanation of olefins has been unsuccessful as yet.

We wish to make a preliminary report on the first synthesis of olefinic cyanides from olefins by means of some metal cyanides.

$$CH_2{=}CHR \xrightarrow[\text{solvent}]{M(CN)_2} CH_2{=}CR{-}CN$$

$$R = H, CH_3$$

In the present study, palladium(II) cyanide, nickel(II) cyanide, and copper(I) cyanide were selected as metal cyanides because of the ability of the metal to π complex with the olefin.

The reaction of ethylene was carried out in an autoclave under 55 kg/cm^2 pressure of ethylene in the presence of the metal cyanide (0.03 mole) and solvent (30 ml) at 150° for 5 hr. The results of cyanation with palladium(II) cyanide in several polar solvents are listed in Table I.

Table I. Cyanation of Ethylene with $Pd(CN)_2$

Solvent	Yield,[a] % Acrylonitrile	Propionitrile
C_6H_5CN	50.8	6.9
CH_3CN	17.2	2.7
DMF	7.7	15.6
DMSO	12.6	2.4

[a] Based on $Pd(CN)_2$ used.

In all cases with the exception of the reaction of copper(I) cyanide, small amounts of polyethylene ranging from gaseous oligomers to crystalline polymers of high molecular weight were always found in addition to the above cyanation products.

Only palladium(II) cyanide among the three metal cyanides was an efficient reagent for the cyanation. Probably this is due to the greater ease with which it forms π complexes with olefins. In the reaction, palladium(II) cyanide is reduced to metallic palladium, and the formation of hydrogen cyanide is observed.

When nonpolar solvents such as cyclohexane and benzene were used, the cyanation was completely repressed, while the polymerization of ethylene took place predominantly to give a large quantity of high polymers.[3] The solvent plays a key role in the cyanation; a more polar solvent accelerates the cyanation. Moreover, in the case of a polar solvent the addition of a highly polarizable nucleophile, such as triphenylphosphine, resulted in a considerable suppression of both cyanation and polymerization of ethylene because such a nucleophile, being a good π-accepting ligand, may block coordination by the ethylene. In addition, with some cyanide complexes such as potassium tetracyanopalladate(II) and potassium tetracyanonickelate(II) in place of metal cyanide, the oligomerization of ethylene occurred to some extent, but the cyanation did not take place at all, no matter what solvent was used.

(2) (a) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern, *Proc. Chem. Soc.*, 111 (1963); (c) E. W. Stern and M. L. Spector, *ibid.*, 370 (1961); (d) J. Tsuji, M. Morikawa, and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4851 (1964).

(3) A. U. Blackham, U. S. Patent 3,194,800 (1965).

A brief survey of the applicability of palladium(II) cyanide to other olefins was made. In the reaction of propylene (0.5 mole) in the presence of palladium(II) cyanide (0.02 mole) and a polar solvent (30 ml) for 5 hr, methacrylonitrile(I), 3-butenenitrile (II), crotononitrile (III), isobutyronitrile (IV), and butyronitrile (V) were obtained, along with a trace of oligomers, consisting mainly of hexene isomers. The results of the cyanation of propylene are listed in Table II.

Table II. Cyanation of Propylene with $Pd(CN)_2$

Solvent	Temp, °C	Yield,[a] % I	II	III	IV	V
C_6H_5CN	150	3.6	0.1	2.5	0.7	0.5
C_6H_5CN	210	20.5	4.5	Trace	6.4	None
DMF	210	20.0	12.0	None	2.5	None
C_2H_5CN	210	22.2	4.5	7.7	None	2.3

[a] Based on $Pd(CN)_2$ used.

As in the case of ethylene, the reaction of propylene in nonpolar solvents such as cyclohexane and benzene led almost exclusively to the formation of high polymers (mp 108–110°). In addition, in the reaction of cyclohexene (0.1 mole) in the presence of palladium(II) cyanide (0.03 mole) and acetonitrile (30 ml) at 130° for 5 hr, 2-cyclohexene-1-carbonitrile (9.43%) and cyclohexane carbonitrile (5.59%) were obtained, along with cyclohexane (7.13%) and benzene (5.71%). In the absence of solvent in the above reaction, the cyanation was somewhat suppressed, while the yields of cyclohexane and benzene were increased extraordinarily to 478 and 212%, respectively. In view of these facts, it may be considered that the cyanation of cyclohexene proceeds through a π-allyl complex.

The mechanism of this unique cyanation is under investigation and detailed description of this and further work will be reported shortly.

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The Stereochemistry of the Carbonyl Insertion Reaction

Sir:

Acetylmanganese pentacarbonyl is formed when carbon monoxide reacts with methylmanganese pentacarbonyl. This reaction is a carbonyl insertion reaction and is a special case of the general reaction: $CH_3Mn(CO)_5 + L \rightarrow CH_3COMn(CO)_4L$, where L is a neutral or charged nucleophile. This generalization is supported by reports that $CH_3Mn(CO)_5$ reacts with amines[1,2] and triphenylphosphine,[2,3] -arsine,[3] or -stibine[3] to form complexes of the type $CH_3COMn(CO)_4L$, and with lithium iodide[4] to give $Li^+[CH_3COMn(CO)_4I]^-$.

(1) K. A. Keblys and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(2) R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, **86**, 3994 (1964).

(3) W. D. Bannister, M. Green, and R. N. Haszeldine, *Chem. Commun.*, 55 (1965).

(4) F. Calderazzo and K. Noak, *J. Organometal. Chem.* (Amsterdam), **4**, 250 (1965).

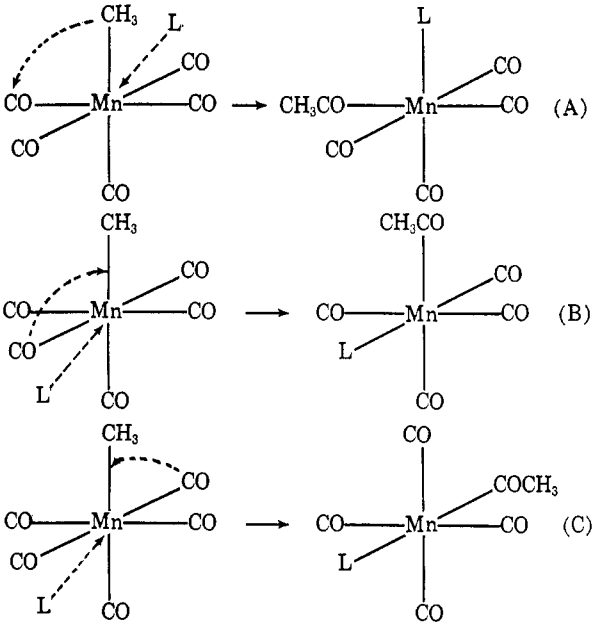
The stereochemistry and hence the mechanism of this type of reaction is, however, rather ill-defined. For example, in the reaction of $CH_3Mn(CO)_5$ with Ph_3P, mixtures of *cis*- and *trans*-$CH_3COMn(CO)_4Ph_3P$ are obtained,[5] and it is not clear whether both isomers are formed by independent reaction paths or whether the reaction is stereospecific and that the other isomer *i.e.*, *cis* or *trans*, is formed in a subsequent thermodynamically controlled step.

The bridgehead phosphites 4-methyl- (or -ethyl-) 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane react at room temperature with methylmanganese pentacarbonyl in methylene chloride or chloroform solution to give in high yield the complexes *cis*-$CH_3COMn(CO)_4L$, where L is $P(OCH_2)_3CCH_3$ or $P(OCH_2)_3CC_2H_5$. This contrasts with the earlier observation[3] that disubstituted complexes $CH_3COMn(CO)_3L_2$ are formed in the reaction of phosphites with $CH_3Mn(CO)_5$.

When the reaction of $CH_3Mn(CO)_5$ with the ligand $P(OCH_2)_3CCH_3$ is followed by observing the proton magnetic resonance spectrum immediately after mixing the reactants and then at suitable time intervals, the peaks at τ 10.1 (singlet, $CH_3Mn(CO)_5$), 9.31 (singlet, $P(OCH_2)_3CCH_3$), and 6.18 (doublet, J = 2 cps, $P(OCH_2)_3CCH_3$) decrease in intensity and are replaced by peaks corresponding to a single isomer at τ 9.18 (singlet, $MnP(OCH_2)_3CCH_3$), 7.58 (singlet, CH_3COMn),[6] and 5.85 (doublet, J = 5.7 cps, $MnP(OCH_2)_3CCH_3$), with final relative integrated intensities of 1:1:2, respectively. The rate of appearance of the new peaks, which was dependent on phosphite concentration, corresponded exactly to the rate of disappearance of the peaks assigned to the reactants. The infrared spectrum of the carbonyl region of the reaction mixture showed the progressive development of four terminal carbonyl bands at 2082 (m), 2008 (s), 1983 (s), and 1972 (s) cm^{-1}, and an acyl band at 1618 (m) cm^{-1} [7] which corresponds to the formation of the complex *cis*-$CH_3COMn(CO)_4[P(OCH_2)_3CCH_3]$ with C_s symmetry.

These observations are of particular interest in that they demonstrate that in the reaction of $CH_3Mn(CO)_5$ with the sterically compact ligand $P(OCH)_3CCH_3$ a stereospecific reaction occurs. It is suggested that each act of substitution gives *cis*-$CH_3COMn(CO)_4[P(OCH_2)_3CCH_3]$ directly. However, an alternative explanation of these results is that *trans*-$CH_3COMn(CO)_4[P(OCH_2)_3CCH_3]$ is formed in a slow step and then undergoes a very fast irreversible rearrangement to the corresponding *cis* isomer. We regard this as unlikely, because it has been shown[5] that *cis*- and *trans*-$CH_3COMn(CO)_4Ph_3P$ rapidly equilibriate in solution, the *trans* isomer predominating, and it is not clear why in the system *trans*-$CH_3COMn(CO)_4[P(OCH)_3CCH_3] \rightleftarrows$ *cis*-$CH_3COMn(CO)[P(OCH_2)_3CCH_3]$ the equilibrium should now be entirely in favor of the *cis* isomer, as would be required by this alternative explanation.

Both Mechanisms, A or B, are both consistent with the observed stereochemistry but mechanism C, which involves insertion of a molecule of CO, previously



bonded *trans* to the point of attack of the ligand on manganese between the methyl group and the manganese, can be excluded, because it would afford the *trans* isomer $CH_3COMn(CO)_4L$.

A kinetic investigation of the transformation

$$trans\text{-}CH_3COMn(CO)_4Ph_3P \overset{-CO}{\rightleftharpoons} cis\text{-}CH_3Mn(CO)_4Ph_3P$$

leads to the proposal[8] that mechanism A, *i.e.*, methyl migration, is preferred to mechanism B. However, the fact that *cis*- and *trans*-$CH_3COMn(CO)_4Ph_3P$ rapidly equilibriate in solution makes such a conclusion of doubtful value.

The complexes *cis*-$CH_3COMn(CO)_4[P(OCH_2)_3CR]$ (R = CH_3 or C_2H_5) decarbonylate slowly on heating to give *cis*-$CH_3Mn(CO)_4[P(OCH_2)_3CR]$.

(5) C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, 87, 5267 (1965).

(6) CH_3COMn protons normally have a chemical shift in the range τ 7.4–7.6.

(7) The reaction mixture was evaporated and the spectrum measured in cyclohexane solution. The evaporated solution on redissolving in $CDCl_3$ showed an unchanged pmr spectrum.

(8) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, 86, 5043 (1964).

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Studies on Polypeptides. XXXV. Synthesis of S-Peptide$_{1-20}$ and Its Ability to Activate S-Protein[1-3]

Sir:

A recent communication by Scoffone, *et al.*,[4] describing a synthesis of 10-ornithine-S-peptide, prompts us to record at this time the synthesis of the eicosapeptide lysylglutamylthreonylalanylalanylalanyllysylphen-

(1) The authors wish to express their appreciation to the U. S. Public Health Service and the American Cancer Society for generous support of this investigation.

(2) The peptides and peptide derivatives mentioned are of the L configuration. In the interest of space conservation the customary L designation for individual amino acid residues is omitted. General conditions for paper and thin layer chromatography are those given in ref 6; *t*-Boc = *t*-butoxycarbonyl; *t*-But = *t*-butyl ester.

(3) See K. Hofmann, F. M. Finn, M. Limetti, J. Montibeller, and G. Zanetti, *J. Am. Chem. Soc.*, 88, 3633 (1966), for paper XXXIV in this series.

(4) E. Scoffone, F. Marchiori, R. Rocchi, G. Vidali, A. Tamburro, A. Scatturin, and A. Marzotto, *Tetrahedron Letters*, No. 9, 943 (1966).