

Reactions of Isocyanides with Alkylpentacarbonylmanganese¹

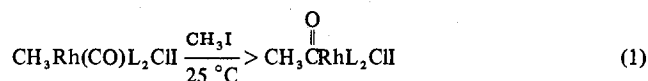
DONALD W. KUTY and JOHN J. ALEXANDER*

Received October 10, 1977

Benzylpentacarbonylmanganese and *p*-chlorobenzylpentacarbonylmanganese react with aliphatic isocyanides *n*-butyl isocyanide, *tert*-butyl isocyanide, and cyclohexyl isocyanide. The products are (phenyl)acetyl- and (*p*-chlorophenyl)acetyltetra-carbonylisocyanidemanganese reflecting carbonylation rather than direct insertion of isocyanide into the Mn-C bond. Similarly methylpentacarbonylmanganese affords acetyltetra-carbonyl(*tert*-butyl isocyanide)manganese. *p*-Nitrobenzylpentacarbonylmanganese is unreactive toward isocyanides. The acyl products are isolated as mixtures of *cis* and *trans* isomers. (*p*-Chlorophenyl)acetyltetra-carbonyl(*tert*-butyl isocyanide)manganese has been thermally decarbonylated to produce exclusively *cis*-*p*-chlorobenzyltetra-carbonyl(*tert*-butyl isocyanide)manganese. When this latter compound is allowed to react with 1-ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane alkyl migration occurs onto coordinated carbon monoxide giving a mixture of *fac* and *mer* isomers of (*p*-chlorophenyl)acetyltricarbonyl(*tert*-butyl isocyanide)(1-ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane)manganese.

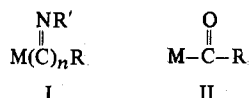
Introduction

Isocyanides, being isoelectronic with carbon monoxide, have recently begun to attract a good deal of attention as ligands in transition-metal complexes.² Because isocyanides are slightly better σ donors and rather comparable π acceptors as measured against CO,³ the possibility exists of controlling fairly sensitively the amount of charge on the metal atom in complexes. Such a feature might be employed to enhance particular reactions taking place in the coordination sphere of the metal while suppressing others. As one example, the rearrangement described by eq 1⁴ takes place at a rate a

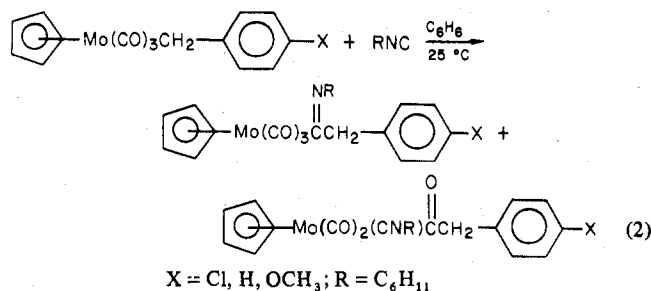


hundredfold smaller when $\text{L} = \text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$ than when $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$. That is, the migration reaction is promoted by less basic phosphines. In contrast, although $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$ readily adds H_2 oxidatively, $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{PF}_3)\text{Cl}$ does not form the dihydride.⁵ The reason is presumably related to the electron-withdrawing effect of PF_3 . When phosphines are employed as ligands, some care must be taken to rule out steric effects.⁶

Because the replacement of carbonyl ligands with isocyanides often leads to essentially no change in structural parameters,⁷ isocyanide-substituted carbonyl complexes should make ideal candidates for studying phenomena dependent on charge density at metals. Interesting complications sometimes arise, however, since isocyanide ligands do not always behave in a simple fashion replacing carbonyls. In particular, a number⁸ of reactions are known leading to the products of isocyanide insertion (sometimes multiple) into metal-carbon bonds, namely, iminoacyl complexes of structure I. These species are, of course, isoelectronic with metal-acyl complexes of structure II when $n = 1$.



An especially interesting case is reaction 2 investigated by



Yamamoto and Yamazaki.^{8a,9} Varying yields of iminoacyl and acyl products were observed with the maximum yield of iminoacyl when $\text{X} = \text{Cl}$. Moreover, it was demonstrated that the isocyanide insertion product arose via some route not involving alkyl migration from CO to isocyanide since it could not be obtained by heating the acyl. This behavior is in contrast to the usual mode of reaction of molybdenum alkyls with nucleophilic reagents L ($\text{L} =$ phosphines,^{10a,b} $t\text{-C}_4\text{H}_9\text{NC}$,^{10c} $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}$)^{10c} leading exclusively to $\eta^5\text{-(C}_5\text{H}_5\text{)-Mo}(\text{CO})_2\text{LC}(\text{O})\text{R}$ and resembles (at least superficially) the reaction with electrophilic sulfur dioxide which leads exclusively to $\eta^5\text{-(C}_5\text{H}_5\text{)-Mo}(\text{CO})_2\text{S}(\text{O})_2\text{R}$,¹¹ the product of direct insertion into the metal-alkyl bond.

As part of a program of research involving isocyanides and their reactions with transition-metal species and because of our interest in insertion reactions we have investigated the behavior of some alkyl manganese pentacarbonyl complexes with isocyanides in order to ascertain whether direct insertion to afford iminoacyls or carbonylation to afford isocyanide-substituted acyls would occur. Similar reactions were previously investigated by Joshi, Pauson and Stubbs¹² who found that methyl- and phenylpentacarbonylmanganese were reduced to substitution products of dimanganese decacarbonyl by phenyl isocyanide in refluxing tetrahydrofuran. Our results, which differ considerably from theirs, are reported here. In particular, acyl complexes are found to be reaction products at room temperature. We also report some preliminary studies on attempts to achieve alkyl migration onto isocyanides coordinated to Mn.

Experimental Section

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., Meade Laboratories, Amherst, Mass., Chemalytics, Inc., Tempe, Ariz., and Integral Microanalytical Laboratories, Raleigh, N.C. Infrared spectra were recorded on a Beckman IR-12 and occasionally on a Perkin-Elmer 337 spectrometer. Solution spectra were taken using 0.1-mm NaCl cells; NaCl plates were employed for Nujol mull spectra. Proton NMR spectra were recorded on a Varian A-60 spectrometer. Me_4Si was used as an integral standard. Carbon-13 NMR spectra were recorded on a Bruker HX-90 spectrometer equipped with a variable-temperature probe. Molecular weights were determined from mass spectra or in chloroform solution on a Hewlett-Packard Model 302B vapor pressure osmometer. Melting points were measured using a Fisher-Johns melting point apparatus and are uncorrected. DTA scans were done on a Perkin-Elmer DSC-18 differential scanning calorimeter. Mass spectra were obtained on an RMU-7 mass spectrometer.

Materials. $\text{CH}_3\text{Mn}(\text{CO})_5$,¹³ $\text{C}_6\text{H}_5\text{CH}_2\text{Mn}(\text{CO})_5$,¹³ CH_3NC ,¹⁴ $t\text{-C}_4\text{H}_9\text{NC}$,¹⁵ $n\text{-C}_4\text{H}_9\text{NC}$,¹⁶ and $\text{C}_6\text{H}_{11}\text{NC}$ ¹⁵ were prepared by standard literature methods. Dimanganese decacarbonyl was purchased from Pressure Chemical Co. 1-Ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane was purchased from Strem Chemicals, Inc. Tetrahydrofuran (THF) was refluxed over CaH_2 and freshly distilled before

Table I. Physical Properties and Analytical Data for Isocyanide Complexes

Compound	Mp, °C	Anal. calcd (found)			Mol wt	% yield
		% C	% H	% other		
CH ₃ C(O)Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉)	Oil	45.1 (42.9)	4.09 (4.35)	4.78 (4.64) (N)	293 (290) ^b	48
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CN- <i>n</i> -C ₄ H ₉)	Oil	55.3 (52.5)	4.34 (4.84)		369 (369) ^a	66
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉)	55-57	55.3 (54.3)	4.34 (5.34)		369 (369) ^a	20
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CNC ₆ H ₁₁)	37-39	57.7 (57.4)	4.56 (5.39)		395 (401) ^b	16
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉)	83-85	50.5 (50.2)	3.72 (3.64)		404 (403) ^b	54
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₄ (CNC ₆ H ₁₁)	51-52	53.1 (52.8)	3.96 (4.21)	8.28 (8.25) (Cl)	429 (441) ^b	46
<i>p</i> -ClC ₆ H ₄ CH ₂ Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉)	46-48	51.1 (49.1)	4.00 (3.68)	9.44 (9.40) (Cl)	375 (375) ^a	39
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₃ (CN- <i>t</i> -C ₄ H ₉)- [P(OCH ₂) ₃ CC ₂ H ₅]	134-137	49.1 (48.5)	4.84 (4.81)	6.60 (6.56) (Cl)	537 (537) ^a	90

^a From mass spectrum. ^b In CHCl₃ solution.

Table II. Infrared Spectral Data^e for Isocyanide Complexes

Compound	Carbonyl stretching freq, cm ⁻¹		Isocyanide stretching freq, cm ⁻¹
	Cis	Trans	
CH ₃ C(O)Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉) ^a	2069 m, A' 1997 sh, A' 1988 s } A', A'' 1973 s } 1649 w, acyl	2069 m, A ₁ 1961 m, E 1649 w, acyl	2186 (m) 2166 (w)
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CN- <i>n</i> -C ₄ H ₉) ^b	2071 m, A' 2012 sh, A' 1990 vs } A', A'' 1977 s } 1629 w, br, acyl	2071 m, A ₁ 1967 s, E 1629 w, br, acyl	2183 (m, br)
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉) ^a	2070 m, A' 1990 s, A' 1980 s, br, A', A'' 1632 w, acyl	2070 m, A ₁ 1966 s, E 1644 w, acyl	2187 (m) 2170 (sh)
C ₆ H ₅ CH ₂ C(O)Mn(CO) ₄ (CNC ₆ H ₁₁) ^a	2068 m, A' 2011 s, A' 1999 s } A', A'' 1988 vs } 1634 w, acyl	2065 m, A ₁ 1974 s, E 1632 w, acyl	2190 (m, br)
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₄ (CN- <i>n</i> -C ₄ H ₉) ^b	2071 m, A' 2013 s, A' 1998 s } A', A'' 1988 vs } 1633 w, br, acyl	2071 m, A ₁ 1975 s, E 1633 w, br, acyl	2179 (m) 2152 (sh)
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₄ (CNC ₆ H ₁₁) ^a	2070 m, A' 2014 m, A' 1999 s } A', A'' 1989 vs } 1638 m, br, acyl	2079 m, A ₁ 1975 s, E 1638 m, br, acyl	2194 (m) 2184 (sh)
<i>p</i> -ClC ₆ H ₄ CH ₂ Mn(CO) ₄ (CN- <i>t</i> -C ₄ H ₉) ^b	2065 m, A' 1999 s, A' 1989 s } A', A'' 1966 s }		2174 (m)
Compound	Carbonyl stretching freq, cm ⁻¹		Isocyanide stretching freq, cm ⁻¹
	Fac	Mer	
<i>p</i> -ClC ₆ H ₄ CH ₂ C(O)Mn(CO) ₃ (CN- <i>t</i> -C ₄ H ₉)[P(OCH ₂) ₃ CC ₂ H ₅] ^c	2018 s 1930 sh 1915 s 1600 w, br, acyl ^d	2060 vw 1956 s 1924 s 1600 w, br, acyl ^d	2192 m 2077 sh

^a Run in hexane solution. ^b Run in heptane solution. ^c Run in Nujol mull. ^d Run in chloroform solution. ^e Key to intensities: w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder.

each use. Technical grade pentane and hexanes were employed as solvents. All other chemicals were reagent grade and were used as received.

p-ClC₆H₄CH₂Mn(CO)₅. This complex was prepared in a manner similar to preparations of other alkyl pentacarbonylmanganese complexes. In a typical synthesis 2.00 g (5.65 mmol) of Mn₂(CO)₁₀ in THF was reduced under N₂ by stirring with 2% sodium amalgam. The amalgam was drained off and the solution of NaMn(CO)₅ added dropwise to a solution of 1.83 g (11.3 mmol) of *p*-ClC₆H₄CH₂Cl in THF at 0 °C. The mixture was allowed to stir under N₂ for 6 h while warming to room temperature. The solvent was then removed at reduced pressure and the residue was extracted with pentane. The extract was filtered through diatomaceous earth. The solution was cooled to -78 °C after reducing the volume; the yellow crystalline

precipitate was collected by suction filtration and sublimed at 80 °C (30 mm) onto a dry ice cooled probe. The yellow crystalline product (mp 79-80 °C) was obtained in 56% yield (1.83 g). The product was identified by its NMR and IR spectra: NMR (CDCl₃) τ 2.87 (s, 4 H), 7.67 (s, 2 H); IR (CCl₄) 2093 (m), 2034 (w), 2012 (vs), 1984 (s) cm⁻¹.

p-O₂NC₆H₄CH₂Mn(CO)₅. This compound was prepared in 47% yield by the above procedure employing *p*-O₂NC₆H₄CH₂Br and omitting the sublimation step. NMR (CDCl₃) τ 2.05 (q, 4 H), 5.43 (s, 2 H); IR (THF) ~2130 (m), 2062 (s), 2026 (vs), 1990 (s) cm⁻¹.

Synthesis of the Isocyanide Complexes. All reactions were carried out under N₂. Physical properties and analytical data are summarized in Table I while spectral data are reported in Tables II and III. Acyl complexes were prepared using the procedures illustrated below for

Table III. NMR Spectral Data for Isocyanide Complexes

Compound	τ (relative intensity) ^e
$\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)^b$	9.20 (10.3), $\text{C}(\text{CH}_3)_3$; 8.30 (3.0), $\text{C}(\text{O})\text{CH}_3$
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-n\text{-C}_4\text{H}_9)^a$	9.4–8.4, complex m (6.62), $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NC}$; 6.72 t (1.70), CH_2NC ; 6.16 (1.96), $\text{CH}_2\text{C}_6\text{H}_5$; 3.02 (5.00), C_6H_5
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)^a$	8.74 (10.6), $\text{C}(\text{CH}_3)_3$; 6.07 (1.86), CH_2 ; 2.77 (5.00), C_6H_5
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CNC}-\text{H}_{11})^c$	8.64–8.30 (10.8), $\text{CH}(\text{CH}_2)_5$; ~6.3 and 6.0 (2.94), $\text{CH}(\text{CH}_2)_5$ and $\text{CH}_2\text{C}_6\text{H}_5$; 2.90 (5.00), C_6H_5
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-n\text{-C}_4\text{H}_9)^a$	8.47 (10.7), $\text{C}(\text{CH}_3)_3$; 6.02 (2.06), CH_2 ; 2.90 (4.00), $\text{C}_6\text{H}_4\text{Cl}$
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CNC}-\text{H}_{11})^a$	8.30 d (9.85), $\text{CH}(\text{CH}_2)_5$ ($^2J = 17.1$ Hz); 6.13 and 5.95 (2.80), $\text{CH}(\text{CH}_2)_5$ and CH_2 ; 2.80 q (4.00), $\text{C}_6\text{H}_4\text{Cl}$
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)^a$	8.48 and 7.74 (10.9), $\text{C}(\text{CH}_3)_3$ and CH_2 ; 2.97 (4.00), $\text{C}_6\text{H}_4\text{Cl}$
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_3(\text{CN}-t\text{-C}_4\text{H}_9)[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]^d$	9.17 m and 8.60 (br, m), (4.90), CH_2CH_3 and CH_2CH_3 ; 8.48 (9.00), $\text{C}(\text{CH}_3)_3$; 5.90 (1.60) CH_2 ; 5.64 d (6.00), $\text{P}(\text{OCH}_2)_3$ ($^3J_{\text{P-H}} = 3.8$ Hz); 2.96 (3.82) q, $\text{C}_6\text{H}_4\text{Cl}$

^a Run in chloroform-*d*. ^b Run neat. ^c Run in carbon tetrachloride. ^d Run in acetone-*d*₆. ^e Key: t = triplet, m = multiplet, d = doublet, q = quartet.

$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$.

$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$. A total of 2.00 g (6.24 mmol) of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$ was dissolved in 15 mL of THF; 0.50 g (6.0 mmol) of $t\text{-C}_4\text{H}_9\text{NC}$ in 10 mL of THF was added dropwise. The solution was stirred at room temperature for 24 h with the flask wrapped to exclude room light. At the end of this time the solvent was removed at reduced pressure. The resulting yellow-brown oil was dissolved in 50:50 v/v CH_2Cl_2 /hexane and chromatographed on grade III acid-washed alumina. Two yellow bands developed; the first was eluted with CH_2Cl_2 /hexane and contained the acyl isocyanide complex along with a trace of unreacted $t\text{-C}_4\text{H}_9\text{NC}$. Upon reducing the volume, enriching in hexanes under a stream of N_2 , and cooling to -78°C , white crystals of the product precipitated. These crystals were collected on a frit, washed with cold hexanes, and recrystallized from boiling hexane. Yield 1.30 g (54%). The second yellow band was eluted with chloroform and contained traces of unreacted isocyanide along with a product identified by IR as a disubstituted acyl complex.¹⁷ With other alkyls and isocyanides repeated chromatographies were often required in order to obtain a crystalline product. $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$ and $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-n\text{-C}_4\text{H}_9)$ were oils at room temperature.

Decarbonylation of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$. A total of 3.00 g (7.00 mmol) of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$ was heated to 110°C under a stream of N_2 until gas evolution ceased (about 15 min). After cooling to room temperature the residue was chromatographed on grade III alumina eluting with 50:50 v/v chloroform/hexane. The first band which contained the product was placed under a stream of N_2 to evaporate the solvent. The resulting yellow oil was dissolved in pentane and cooled to -78°C to precipitate the product which was then recrystallized twice from boiling hexane. Yield 1.70 g (57%). A second yellow band contained product and $t\text{-C}_4\text{H}_9\text{NC}$ while a third band eluted with acetone gave a trace of a product whose infrared spectrum indicated the presence of a disubstituted alkyl.

Synthesis of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_3(\text{CN}-t\text{-C}_4\text{H}_9)[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]$. A mixture of 0.30 g (0.80 mmol) of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$ and 0.13 g (0.80 mmol) of 1-ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane in 10 mL of THF was stirred for 24 h at room temperature. The solvent was removed at reduced pressure and the crude compound recrystallized from chloroform/hexane to give 0.40 g (90%) of the white crystalline product.

Results and Discussion

Preparation of the Acyl Complexes. The reactions of aliphatic isocyanides with methyl-, benzyl-, and *p*-chlorobenzylpentacarbonylmanganese were best carried out employing a 10% or so excess of the manganese complex in order to consume the isocyanide as completely as possible. The progress of the reactions could be conveniently followed by observing the disappearance of the $\text{C}\equiv\text{N}$ stretching frequency of the free isocyanides ($\sim 2110\text{--}2150\text{ cm}^{-1}$) and the growing in of the $\text{C}\equiv\text{N}$ frequency of the coordinated isocyanides ($\sim 2170\text{ cm}^{-1}$). Completion was generally attained in about 10 or 12 h by this criterion. Even though an excess of the manganese carbonyl was always employed, the purification and crystallization of the products were rendered extremely difficult perhaps owing to traces of unreacted isocyanide which was not spectroscopically detectable (but the odor of which was apparent) or to the presence of an isomer mixture. Several different solvents and solvent combinations were tried for the chromatography on alumina: chloroform, chloroform-hexane, hexane, pentane, dichloromethane, dichloromethane-hexane, and even carbon tetrachloride. None of these gave really satisfactory separation of unreacted isocyanide although dichloromethane-hexane seemed to work best. Sometimes several chromatographies were needed before crystals could be isolated from the resulting solutions upon concentration and cooling. Often the crystallizations required several days at -78°C . We were most successful in obtaining crystals when *tert*-butyl isocyanide was employed.

Other difficulties also contributed to the rather low yields. Prolonged exposure to room light initiated a photochemical process producing a brown coloration in solutions; the presence of this impurity made crystallization more difficult. It was impossible to remove all the product complex from the alumina column; the difficulty increased as the compounds became purer and, hence, less soluble. Finally, formation of small amounts of disubstitution products sometimes diverted a fraction of the manganese starting material. These products were identified by their infrared spectra as a mixture of *fac* and *mer* isomers. No reactions occurred with $p\text{-(O}_2\text{N)-C}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$. This is in keeping with observations of Calderazzo and Noack¹⁸ who found that electron-withdrawing alkyl groups retarded the carbonylation reactions of $\text{RMn}(\text{CO})_5$ with various ligands.

Properties and Characterization of Acyl Complexes.

General. The isocyanide-substituted acyl and alkyl complexes were white solids with the exception of $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-t\text{-C}_4\text{H}_9)$ and $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN}-n\text{-C}_4\text{H}_9)$ which were yellow oils. It is likely that the latter compound should have a melting point above room temperature but that our efforts to obtain crystals were frustrated by the presence of small quantities of the high-boiling $n\text{-C}_4\text{H}_9\text{NC}$ or perhaps by the isomer mixture.

Infrared Spectra. The infrared stretching frequencies of the products clearly demonstrate that alkyl isocyanides react to give products of carbonyl insertion and not the iminoacyls of isocyanide insertion into the manganese-alkyl bond. Table II reports the spectra of the products. The appearance of bands in the $2150\text{--}2180\text{-cm}^{-1}$ region indicates the presence of terminal isocyanide ligands. Shifts of the $\text{C}\equiv\text{N}$ stretching frequencies to higher energy by some $30\text{--}50\text{ cm}^{-1}$ on coordination are similar to those seen for manganese(I) complexes *cis*- $\text{Mn}(\text{CO})_4(\text{CNCH}_3)\text{X}$ ($\text{X} = \text{CH}_2\text{CN}$, $\text{Ge}(\text{C}_6\text{H}_5)_3$, $\text{Sn}(\text{C}_6\text{H}_5)_3$, $\text{Pb}(\text{C}_6\text{H}_5)_3$, HgI)¹⁹ and *cis*- $\text{Mn}(\text{CO})_4(\text{CNCH}_3)\text{Br}$.²⁰

The weak band in the $1630\text{--}1650\text{-cm}^{-1}$ region of each of the spectra is attributable to $\text{C}=\text{O}$ rather than $\text{C}=\text{N}$ stretching. In our compounds the presence of a single isocyanide as shown by analytical and molecular weight data as

well as the observation of $\nu_{\text{C}=\text{N}}$ leaves assignment of the 1630–1650-cm⁻¹ bands to $\nu_{\text{C}=\text{O}}$ as the only possibility.

The spectra of these isocyanide-substituted acyl compounds in the terminal CO stretching region make it clear that the samples are mixtures of cis and trans isomers. Assignments are given in Table II. As was found previously²¹ to be the case for $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]$ the highest energy A' band of the cis isomer is assigned as coincident with the A₁ band of the trans isomer. The relative amounts of cis and trans isomers present at equilibrium would seem to be rather similar for the *tert*-butyl and cyclohexyl isocyanide ligands presumably for steric reasons. The positions of the terminal stretching frequencies are ~ 20 cm⁻¹ higher than those for analogous bands in triphenylphosphine-substituted acyls reflecting the greater π acidity of the isocyanides.

Ordinarily the isocyanide and acyl absorbances are not resolved into separate bands for the two isomers. Some complexes exhibit shoulders on the isocyanide bands which could be assigned to different isomers or to rotamers arising from hindered rotation of the $\text{C}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-X}$ group around the Mn–C bond.

NMR Spectra. The proton NMR spectra of the acyl compounds are consistent with the proposed structures. Considerable broadening (compared to the free ligands) of peaks assigned to coordinated isocyanides is a notable feature of these spectra. Broad signals from the cyclohexyl protons have been noted in other transition metal–isocyanide complexes.^{8d,22} Perhaps the partial overlap of signals from the two geometric isomers contributes to the width of the lines. Also, traces of the free ligand may lead to overlapping signals. In a few cases, the relative intensities of isocyanide proton signals seemed somewhat large even though the elemental analyses were acceptable.

The ¹H NMR line width prevented an assay of the relative amounts of each isomer present at equilibrium in the isolated products. However, the ¹³C NMR spectrum of *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉) in 1,2-dichloroethane at ~ 27 °C displayed two methylene carbon peaks of approximately 60:40 relative area presumably reflecting the cis:trans ratio. After approximately 30 min a new methylene peak corresponding to the decarbonylation product *p*-ClC₆H₄CH₂Mn(CO)₄(CN-*t*-C₄H₉) was observed. Facile decarbonylation in solution may also contribute to the wide lines seen in ¹H NMR spectra by providing an additional impurity in small amounts. The isomer mixture undoubtedly arises from carbonylation of the alkyl to give a cis acyl derivative which subsequently rearranges to the cis–trans population characteristic of the equilibrium. An equimolar mixture of CH₃NC and *p*-ClC₆H₄CH₂Mn(CO)₅ was followed by NMR in both CS₂ and THF. Both solutions showed a gradual decrease in intensity of the benzyl methylene resonance around τ 7.6 and the increase in intensity of a product methylene resonance at around τ 6.0. When the reaction is roughly 20% complete the signal at τ 6.0 begins to split into two signals evidently due to the production of the second product isomer. After 20 h, the signals are sufficiently broadened that no more splitting is detectable. Such behavior is consistent with an alkyl migration step followed by attack of the isocyanide to afford a cis isomer and its slow rearrangement. Noack, Ruch, and Calderazzo have shown²¹ by separating and identifying the isomers that the same mechanism is involved in the reaction of P(C₆H₅)₃ with CH₃Mn(CO)₅. Although we have no independent evidence that the initial product signal is due to the cis isomer, we postulate this assignment in analogy to the results of Noack et al.

Mass Spectra. Mass spectra of three acyl complexes were obtained: *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁), C₆H₅CH₂C(O)Mn-

(CO)₄(CN-*n*-C₄H₉). All three compounds exhibited a peak of highest *m/e* which corresponded to loss of CO from the parent compound. Two major fragmentation pathways are evident, the first being stepwise loss of CO giving finally RMn(CNR')⁺. The second corresponds to initial loss of the alkyl group to afford Mn(CO)₄(CNR')⁺ which then undergoes stepwise loss of CO culminating in the Mn(CNR')⁺ moiety. Preferential loss of CO has previously been observed in some iron carbonyls containing isocyanide ligands.^{8d}

Aside from these common patterns, some differences are apparent depending on the particular complex. The nature of the fragment of highest relative intensity (*ri*) changes with the nature of the alkyl group as well as with the nature of the isocyanide. With C₆H₅CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), the fragment C₇H₇Mn(CNC₄H₉)⁺ is most abundant while with *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), ClC₇H₆Mn⁺ has highest *ri*. The fragment Mn(CO)₂(CNC₆H₁₁)⁺ resulting from alkyl loss is most abundant in the spectrum of *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁).

The spectrum of *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁) displays a set of peaks of *ri* 53 corresponding to the composition ClC₇H₆Mn(CO)⁺ resulting from the loss of two CO's and an isocyanide from the fragment of *m/e* 373. Loss of isocyanide in preference to CO has not been previously observed in the reported mass spectra of iron or manganese compounds.^{8d,22} The other fragment arising from the *m/e* 373 one corresponds to the loss of three CO's giving ClC₇H₆Mn(CNC₆H₁₁)⁺ of *ri* 63. Loss of these fragments may be stepwise or concerted. No metastable peaks corresponding to either kind of process were seen. The simultaneous loss of two CO's from organometallic species²³ has been previously observed.

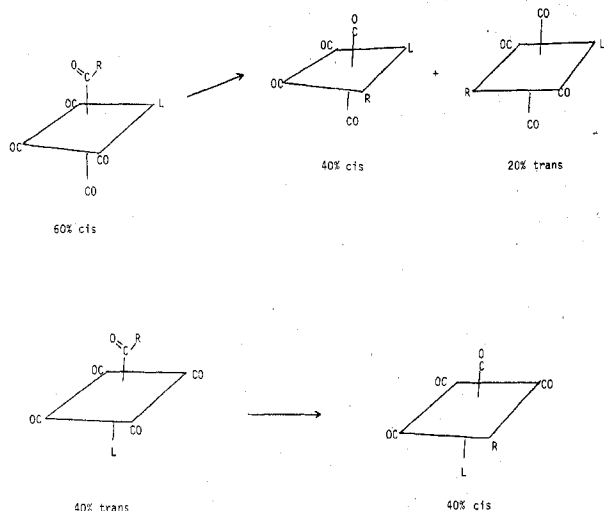
In complexes of *n*-C₄H₉NC and *t*-C₄H₉NC, olefin elimination from Mn(CNR')⁺ gives some Mn(CNH)⁺. However, no olefin elimination occurs when R' = C₆H₁₁. These Mn-containing RMn(CNR')⁺ ions also fragment to give a variety of organic species including R⁺, RH⁺, and C₇H₇⁺ as well as Mn⁺.

Decarbonylation of *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉). The fact that treatment of alkyl pentacarbonylmanganese with aliphatic isocyanides resulted in carbonylation rather than direct isocyanide insertion into the Mn–C bond reflects a pattern of reactivity for these Mn complexes now well established with a wide variety of nucleophilic ligands including CO, phosphines, phosphites, amines, and arsines.²⁴ As contrasted with Mo alkyl species the Mn alkyls display a marked preference for migration of the alkyl group onto a ligand already in the coordination sphere of the metal.

Hence, we decided to undertake a study of the migration of alkyl groups onto coordinated CO and CNR and the factors which control such reactions. We selected *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉) as the starting point for these investigations since it is comparatively easy to synthesize. Heating the cis–trans mixture of this compound to 110 °C in the solid state under N₂ and subsequent chromatography on alumina with chloroform–hexane gave a product which analyzed correctly for *p*-ClC₆H₄CH₂Mn(CO)₄(CN-*t*-C₄H₉). The infrared spectrum of this compound reported in Table II indicates that the cis isomer was the exclusive product. Moreover, the ¹³C NMR spectrum of a 1,2-dichloroethane solution of the acyl compound showed the appearance with time of only a single peak in the methylene region due to the alkyl product over a period of an hour. Similarly, a ¹H NMR spectrum of the acyl in this same solvent shows the appearance of a single product methylene peak at $\tau \sim 8.0$ due apparently to the cis isomer. The peak begins to split detectably after about 6 h as the alkyl isomers equilibrate.

On a statistical basis (see Scheme I) one would anticipate a 4:1 cis:trans product ratio starting from a 60:40 cis:trans

Scheme I



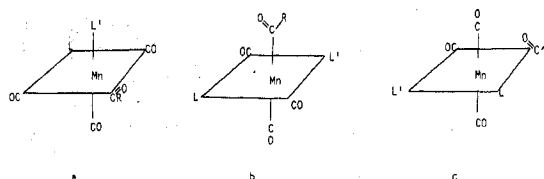
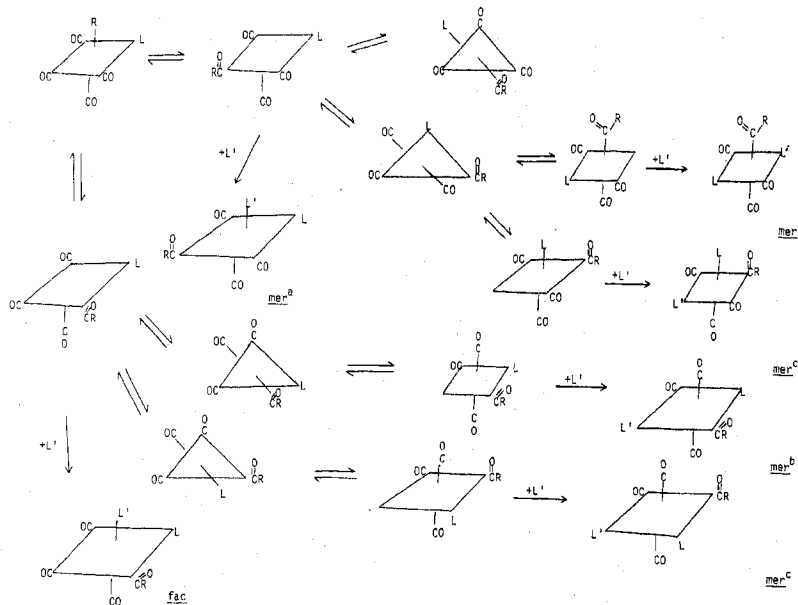
mixture of the acyl and assuming alkyl migration and assuming that both isomers decarbonylate with comparable ease. If this latter assumption were correct, any trans alkyl initially produced could have remained undetected conceivably. The isolation of the pure cis isomer can more likely be ascribed to the deactivating effect of isocyanide on dissociation of the CO trans to it²⁵ thus preventing conversion of any of the cis acyl to trans alkyl under our experimental conditions.

No evidence for loss of the *tert*-butyl isocyanide ligand on pyrolysis was obtained. That is, no $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$ was detected. A trace of what seemed to be a disubstituted alkyl was obtained and identified by its infrared spectrum. Presumably the required isocyanide resulted from complete decomposition of a quantity of the monosubstituted species.

Adams¹⁹ has recently prepared a series of $\text{RMn}(\text{CO})_4(\text{CNCH}_3)$ compounds where $\text{R} = \text{CH}_2\text{CN}$, GeX_3 , SnX_3 , HgX , etc., from the reactions of $\text{Mn}(\text{CO})_4(\text{CNCH}_3)^-$ (prepared in situ) with appropriate halides. Reactions with alkyl halides were not reported although interesting products did result^{8f,g,h} from the reaction between $\eta^5\text{-(C}_5\text{H}_5\text{)Mo}(\text{CO})_2(\text{CNCH}_3)^-$ and CH_3I .

Reactions of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CN-}t\text{-C}_4\text{H}_9)$ with P Donors. We next investigated the reaction of *cis-p*-

Scheme II

Figure 1. Meridional isomers of $\text{RC}(\text{O})\text{Mn}(\text{CO})_3\text{L}(\text{CNR}')$.

$\text{ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CN-}t\text{-C}_4\text{H}_9)$ with triphenylphosphine in order to ascertain whether preferential migration of the alkyl group would occur onto CO or $t\text{-C}_4\text{H}_9\text{NC}$. When equimolar quantities of these compounds were stirred at room temperature in THF no reaction had occurred after 11 h. When the solution was refluxed, a yellow crystalline product was deposited over a period of 24 h. It was too insoluble for characterization by NMR or solution IR; however, in Nujol it displayed three broad strong bands at 1992, 1889, and 1588 cm^{-1} . There were no absorptions in the $\text{C}\equiv\text{N}$ stretching region.

Chromatography of the remaining solution afforded a red oil which had an infrared spectrum appropriate for $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_3(\text{CN-}t\text{-C}_4\text{H}_9)[\text{P}(\text{C}_6\text{H}_5)_3]$; that is, a terminal $\text{C}\equiv\text{N}$ stretch was still present around 2140 cm^{-1} . Any acyl or iminoacyl product formed at this elevated temperature presumably suffered decarbonylation and alkyl migration giving a product containing only terminal isocyanide and carbonyl ligands.

On the supposition that steric repulsions were responsible for the lack of reactivity of triphenylphosphine at room temperature we selected 1-ethyl-3,5,8-trioxa-4-phosphabicyclo[2.2.2]octane as a ligand with a considerably smaller Tolman cone angle similar to that of the 1-methyl analogue.²⁶ From the room temperature reaction of the cage phosphite with *cis-p*- $\text{ClC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CN-}t\text{-C}_4\text{H}_9)$ was isolated white $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_3(\text{CN-}t\text{-C}_4\text{H}_9)[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]$. The presence of the terminal $\text{C}\equiv\text{N}$ stretch in the product at 2192 cm^{-1} shows clearly that alkyl migration to a carbonyl ligand occurred in preference to migration to an isocyanide. The terminal CO stretching region reveals the presence of both *fac* and *mer* isomers.²⁷ As Scheme II shows, simple alkyl migration followed by occupation of the vacated coordination site by phosphite = L would lead to the expectation that the *fac-mer* ratio should be 2:1. Furthermore,

only one of the three possible *mer* isomers depicted in Figure 1 would be produced. Scheme II also shows that rearrangement of intermediates could lead to a greatly enhanced *mer* population. Carbonyl insertion mechanism leads to the same predicted isomer distribution.

The infrared spectrum of the isomer mixture reported in Table II shows the presence of only four C=O bands plus a shoulder in Nujol. Poor solubility prevented measurement of the spectrum in nonpolar solvents such as hexane. In chloroform solution the resolution was poor. The spectrum requires the presence of at least two isomers since only three carbonyl stretches can result from a tricarbonyl complex. The most straightforward possibility would be the presence of a mixture of *fac* and *mer*^a isomers arising as shown in Scheme II. The spectra are assigned on this basis in Table II. The assignments give band patterns for *fac* and *mer* isomers analogous to those obtained by Kraihanzel and Maples²⁷ for some bis(phosphine)-acyl complexes. Note also the two isocyanide absorptions. NMR in acetone-*d*₆ does not display separate signals for each isomer, thus precluding population analysis. Obviously, our results do not rule out the possibility that the two other meridional isomers *mer*^b and *mer*^c may be produced via the paths indicated in Scheme II. It is not clear that these isomers, if present, would have band positions very different from those of *mer*^a. It might be noted, however, that the bands are quite sharp in Nujol suggesting the absence of species with almost overlapping absorptions.

The probable presence of both facial and meridional isomers contrasts with the behavior of disubstituted manganese acetyls containing two phosphine ligands studied by Kraihanzel and Maples.²⁷ These workers found exclusively *mer* or exclusively *fac* isomers of the compounds CH₃C(O)Mn(CO)₃L₂ where L is a phosphine. The balance of steric and electronic requirements of the isocyanide and phosphite ligands is apparently suitable for stabilization of both isomers.

The point of major significance here, though, is that migration of the alkyl group occurs preferentially and exclusively to a coordinated carbonyl rather than to a coordinated isocyanide in the manganese complex. Whether this behavior is general for isocyanide-substituted alkylmanganese complexes remains to be seen. If so, it may be related to the observation²⁴ that migration onto CO in RMn(CO)₅ complexes is retarded by electron-withdrawing R groups. The electron-withdrawing *p*-ClC₆H₄CH₂ group may lead to a large activation energy for a pathway involving Mn-C bond breaking and bond formation between the alkyl and a relatively electron-poor isocyanide. Of interest here are the calculations of Sarapu and Fenske^{3b} which reveal that the electron population in ligand σ and π* HOMO's is higher for *cis* and *trans* CO's than for CNCH₃ in Mn(CO)₅(CNCH₃)⁺. If such a feature carries over to the electronic structure of neutral alkyl complexes, it is plausible that bond formation involving a more highly populated HOMO leads to carbonyl insertion. This would lead to the prediction that isocyanide insertion would be favored relative to CO insertion by more nucleophilic isocyanide and a less electrophilic alkyl group.

On the other hand, it may simply be that the bulky *tert*-butyl group prevents migration onto the isocyanide for steric reasons. Some evidence favoring this view is the presence of appreciable quantities of less crowded *trans* and *mer* isomers of compounds containing *tert*-butyl isocyanide. It is worth noting also that attempted carbonylation of η⁵-(C₅H₅)Fe(CO)[CNC(CH₃)₃]R (R = C₆H₅, C₆H₅CH₂) gives no reaction^{8d} even though analogous complexes with different isocyanides afford the iminoacyl products η⁵-(C₅H₅)Fe(CO)₂[C(R)=NR].

Acknowledgment. Financial support from The Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully

acknowledged. Grant No. GP-8490 from the National Science Foundation enabled the Department of Chemistry at the University of Cincinnati to purchase the RMU-7 mass spectrometer. Mr. Roger Hurst kindly obtained several mass spectra. We thank Professor Milton Orchin for the use of the differential scanning calorimeter.

Registry No. CH₃C(O)Mn(CO)₄(CN-*t*-C₄H₉), 66008-04-6; C₆H₅CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), 66008-03-5; C₆H₅CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), 65982-63-0; C₆H₅CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 65982-62-9; *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), 65982-61-8; *p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 65982-60-7; *p*-ClC₆H₄CH₂Mn(CO)₄(CN-*t*-C₄H₉), 65982-59-4; *p*-ClC₆H₄CH₂C(O)Mn(CO)₃(CN-*t*-C₄H₉)[P(OCH₂)₃CC₂H₅], 65982-58-3; *cis*-CH₃C(O)Mn(CO)₄(CN-*t*-C₄H₉), 66008-02-4; *trans*-CH₃C(O)Mn(CO)₄(CN-*t*-C₄H₉), 65982-57-2; *cis*-C₆H₅CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), 65982-56-1; *trans*-C₆H₅CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), 66008-49-9; *cis*-C₆H₅CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), 66008-48-8; *trans*-C₆H₅CH₂C(O)Mn(CO)₄(CN-*t*-C₄H₉), 66008-47-7; *cis*-C₆H₅CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 66008-51-3; *trans*-C₆H₅CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 66008-50-2; *cis*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), 65995-65-5; *trans*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CN-*n*-C₄H₉), 66008-55-7; *cis*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 66008-54-6; *trans*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₄(CNC₆H₁₁), 66008-53-5; *cis*-*p*-ClC₆H₄CH₂Mn(CO)₄(CN-*t*-C₄H₉), 66008-52-4; *fac*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₃(CN-*t*-C₄H₉)[P(OCH₂)₃CC₂H₅], 66008-08-0; *mer*-*p*-ClC₆H₄CH₂C(O)Mn(CO)₃(CN-*t*-C₄H₉)[P(OCH₂)₃CC₂H₅], 66008-07-9; CH₃Mn(CO)₅, 13601-24-6; C₆H₅CH₂Mn(CO)₅, 14049-86-6; *p*-ClC₆H₄CH₂Mn(CO)₅, 65982-69-6; *p*-O₂NC₆H₄CH₂Mn(CO)₅, 65982-68-5.

References and Notes

- Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept 1976.
- P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973).
- (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 712; (b) A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, **14**, 247 (1975).
- I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).
- D. A. Clement and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 2553 (1972).
- See, for example, T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).
- R. D. Adams, M. Brice, and F. A. Cotton, *J. Am. Chem. Soc.*, **95**, 6594 (1973).
- (a) For a recent review, see Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, **8**, 225 (1972); (b) G. van Kotten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 59 (1972); (c) P. M. Treichel and K. P. Wagner, *J. Organomet. Chem.*, **61**, 415 (1973); (d) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **13**, 2145 (1974); (e) S. Otsuka and K. Ataka, *J. Chem. Soc., Dalton Trans.*, 327 (1976); (f) R. D. Adams and D. F. Chodosh, *J. Am. Chem. Soc.*, **98**, 5391 (1976); (g) *J. Organomet. Chem.*, **122**, C11 (1976); (h) *J. Am. Chem. Soc.*, **99**, 6544 (1977).
- Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*, **24**, 717 (1970).
- (a) G. Capron-Cotigny and R. Poilbanc, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **263**, 885 (1963); (b) K. W. Barnett, *Inorg. Chem.*, **8**, 2009 (1969); (c) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **43**, 143 (1973).
- M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organomet. Chem.*, **16**, 507 (1969).
- K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organomet. Chem.*, **1**, 51 (1963).
- R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).
- J. Casanova, Jr., R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963).
- I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim, and F. Rosendahl, "Organic Syntheses", Collect. Vol., Vol. V, H. Baumgarten, Ed., Wiley, New York, N.Y., 1973, p 300.
- H. L. Jackson and B. C. McKusick, "Organic Syntheses", Collect. Vol., Vol. IV, N. Rabjohn, Ed., Wiley, New York, N.Y., 1963, p 438.
- J. P. Williams and J. J. Alexander, unpublished results.
- F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).
- R. D. Adams, *Inorg. Chem.*, **15**, 174 (1976).
- P. M. Treichel, G. E. Direen, and H. J. Mueh, *J. Organomet. Chem.*, **44**, 339 (1972).
- K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968).
- Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).
- J. Muller and M. Herberhold, *J. Organomet. Chem.*, **13**, 399 (1968).
- A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).
- J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).
- C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
- P. K. Maples and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **90**, 6645 (1968).