The metal complexes of the aziridinophosphines I and II described in this paper were prepared in order to evaluate their potential as alkylating agents in cancer chemotherapy. Alkylating properties for the selected aziridinophosphine complexes $(C_2H_4N)_3PM(CO)_5$ (M = Cr, Mo) and $[(C_2H_4N)_3P]_2PdCl_2$ were demonstrated by positive γ-(4-nitrobenzyl)-pyridine (NBP) tests.[17] The compounds described in this paper were screened for activity against L-1210 lymphoid leukemia in BDF_1 mice. The metal complexes of tris(aziridino)phosphine (Table I) were found to be ineffective. The metal carbonyl complexes $(C_2H_4N)_3PM(CO)_5$ (M = Cr, Mo) were ineffective at doses below 100-200 mg/kg. At larger doses (*e.g.*, 400 mg/kg) these compounds were toxic such that the mean survival time was drastically reduced. The compounds $[(C_2H_4N)_3P]_2MX_2$ (M = Pd, X = Cl; M = Pt, X = Cl, I) exhibited similar behavior, but their toxic doses were somewhat lower (<100 mg/kg).

Preliminary antileukemia screening of the metal complexes of bis(aziridino)morpholinophosphine (II) has been more encouraging. The molybdenum carbonyl complex $(C_2H_4N)_2P(NC_4H_8O)Mo(CO)_5$ was nontoxic even in doses of 400 mg/kg and lengthened the mean survival time by 9-48% at such doses. The metal(II) halide complexes $[(C_2H_4N)_2P(NC_4H_8O)]_2MX_2$ (M = Pd, X = Cl; M = Pt, X = Cl, I) were somewhat more toxic (lethal doses below 100 mg/kg) but lengthened the mean survival time by up to 21% at doses appreciably below the lethal doses. These results, although still too fragmentary to draw any definite conclusions, suggest that appropriate metal complexes of bis(aziridino)morpholinophosphine (II) could be of value in cancer chemotherapy. Considerably more work is needed in order to establish any relationships between structure and antileukemia activity in bis(aziridino)morpholinophosphine (II)-metal complexes.

Acknowledgment. We are indebted to the National Cancer Institute for partial support of this work under Grant CA-12938-01 and to the Deutsche Forschungsgemeinschaft for a fellowship to O. v. S. We thank Dr. J. C. Cloyd, Jr., for running the far-infrared spectra. We thank the Dow Chemical Co. for generous samples of aziridine (ethylenimine). Finally, we thank the Chemotherapy Section of the Drug Research and Development Department of the National Cancer Institute for screening the metal complexes of the aziridinophosphines for activity against L-1210 lymphoid leukemia.

Registry No. Phosphorus trichloride, 7719-12-2; morpholine, 110-91-8; morpholinodichlorophosphine, 932-74-1; aziridine, 151-56-4; bis(aziridino)morpholinophosphine, 51934-12-4; molybdenum hexacarbonyl, 13939-06-5; chromium hexacarbonyl, 13007-92-6; tungsten hexacarbonyl, 14040-11-0; $C_2H_4NHW(CO)_5$, 51213-57-1; $(C_6H_5CN)_2PdCl_2$, 14220-64-5; $(C_6H_5CN)_2PtCl_2$, 14873-63-3; $[(C_2H_4N)_2P(NC_4H_8O)]_{1.5}PdI_2$, 52002-82-1; $(CH_3CN)_2NiCl_2$, 14515-46-9; $(C_2H_4N)_3PCr(CO)_5$, 51933-84-7; $(C_2H_4N)_3PMo(CO)_5$, 51933-85-8; $[(C_2H_4N)_3P]_2PdCl_2$, 51933-86-9; *cis*-$[(C_2H_4N)_3P]_2PtCl_2$, 52022-23-8; $[(C_2H_4N)_3P]_2PtI_2$, 51933-87-0; $(C_2H_4N)_2P(NC_4H_8O)Mo(CO)_5$, 51933-88-1; *cis*-$[(C_2H_4N)_2P(NC_4H_8O)]_2PdCl_2$, 51933-89-2; *cis*-$[(C_2H_4N)_2P(NC_4H_8O)]_2PtCl_2$, 52022-24-9; $[(C_2H_4N)_2P(NC_4H_8O)]_2PtI_2$, 52022-25-0; $[(C_2H_4N)_3P]_2NiCl_2$, 52002-81-0; $(C_2H_4N)_3PNiCl_2$, 52002-77-4; $[(C_2H_4N)_3P]_2ZnCl_2$, 52002-80-9; $(C_2H_4N)_2P(NC_4H_8O)ZnCl_2$, 52002-79-6.

[17] J. Epstein, R. W. Rosenthal, and R. J. Ess, *Anal. Chem.*, 27, 1435 (1955).

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Isocyanide-Metal Complexes. IV. Reactions of Allylbis(acetonitrile)chlorodicarbonylmolybdenum with Various Isocyanides[1,2]

R. B. KING* and MOHAN SINGH SARAN[3]

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Alkyl isocyanides rapidly replace at room temperature the two acetonitrile ligands in $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ to form $C_3H_5Mo(CO)_2(RNC)_2Cl$ (R = methyl, ethyl, isopropyl, *tert*-butyl, neopentyl, cyclohexyl). The course of further reaction depends upon the specific alkyl isocyanide. Thus *tert*-butyl isocyanide forms successively $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ and $[(Me_3CNC)_4MoCl]_2$ whereas methyl and ethyl isocyanides form ultimately *cis*-$(RNC)_4Mo(CO)_2$ (R = CH_3, C_2H_5). Proton nmr spectra on alkyl isocyanide complexes of the types *cis*-$(RNC)_4Mo(CO)_2$ and $C_3H_5Mo(CO)(RNC)_3Cl$ indicate that the chemical shifts of the protons on the β-carbon atom of the alkyl isocyanide ligand are much more sensitive to changes in the environment of the alkyl isocyanide ligand than the chemical shifts of the protons on either the α- or γ-carbon atoms.

Introduction

Recently we reported[4] a spectroscopic study of *tert*-butyl isocyanide derivatives of the octahedral metal carbonyls. For this work as many as possible of the octahedral metal carbonyl derivatives with various numbers of carbonyl groups replaced by *tert*-butyl isocyanide ligands were required. The octahedral *tert*-butyl isocyanide-metal carbonyl complexes obtained from *tert*-butyl isocyanide and the octahedral metal carbonyls, their acetonitrile complexes, and their olefin complexes were successfully used for this spectroscopic study.

The work of tom Dieck, Friedel, and Renk[5,6] suggested that reductive elimination of allyl chloride from the complex[7] $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ on treatment with *tert*-butyl isocyanide might provide an alternate route to some of the required octahedral metal carbonyl complexes. How-

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[1] Part III: R. B. King and M. S. Saran, *Inorg. Chem.*, 13, 364 (1974).

[2] A portion of this work was presented at the 25th Southeastern Regional Meeting of the American Chemical Society, Charleston, S. C., Nov 1973; see Abstracts, No. 286.

[3] Postdoctoral research associate.

[4] R. B. King and M. S. Saran, *Inorg. Chem.*, 13, 74 (1974).

[5] H. tom Dieck and H. Friedel, *J. Organometal. Chem.*, 14, 375 (1968).

[6] H. Friedel, I. W. Renk, and H. tom Dieck, *J. Organometal. Chem.*, 26, 247 (1971).

[7] R. G. Hayter, *J. Organometal. Chem.*, 13, P1 (1968).

Table I. Reactions of $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ with Various Isocyanides

Quantity of $C_3H_5Mo(CO)_2$-$(CH_3CN)_2Cl$, g (mmol)	Isocyanide[a] (ml)	Solvent[b] (ml)	Temp, °C	Time, hr	Product (g, mmol)
0.62 (2.0)	MeNC (1.0)	CH_2Cl_2 (50)	25	~0.1	$C_3H_5Mo(CO)_2(MeNC)_2Cl$ (0.55, 1.77)[c]
0.62 (2.0)	MeNC (1.0)	Hexane (70)	25	15	$C_3H_5Mo(CO)_2(MeNC)_2Cl$ (0.6, 1.93)[c]
0.62 (2.0)	MeNC (2.0)	Hexane (70)	69	5	*cis*-$(MeNC)_4Mo(CO)_2$ (0.11, 0.35)[d]
0.62 (2.0)	MeNC (2.0)	THF (60)	67	0.5	Decomposition
0.3 (1.0)	EtNC (0.5)	CH_2Cl_2 (25)	25	~0.1	$C_3H_5Mo(CO)_2(EtNC)_2Cl$[e]
1.24 (4.0)	EtNC (4.0)	CH_2Cl_2 (60)	25	72	*cis*-$(EtNC)_4Mo(CO)_2$ (0.145, 0.39)[d]
0.62 (2.0)	EtNC (1.0)	Hexane (60)	69	6	Decomposition
0.3 (1.0)	*i*-PrNC (0.5)	CH_2Cl_2 (25)	25	~0.1	$C_3H_5Mo(CO)_2(i\text{-PrNC})_2Cl$[e]
0.31 (1.0)	*t*-BuNC (1.0)	CH_2Cl_2 (15)	25	~0.1	$C_3H_5Mo(CO)_2(t\text{-BuNC})_2Cl$ (0.375, 0.95)[c]
0.31 (1.0)	*t*-BuNC (1.0)	Hexane (50)	25	15	$C_3H_5Mo(CO)(t\text{-BuNC})_3Cl$ (0.4, 0.89)[c]
1.24 (4.0)	*t*-BuNC (2.0)	Hexane (75)	69	12	$C_3H_5Mo(t\text{-BuNC})_4Cl$ (?)[c,f]
0.93 (3.0)	*t*-BuNC (3.0)	MCH (80)	101	24	$[(t\text{-BuNC})_4MoCl]_2$ (1.1, 1.19)[c]
1.24 (4.0)	*neo*-PentNC (2.0)	CH_2Cl_2 (50)	25	~0.1	$C_3H_5Mo(CO)_2(neo\text{-PentNC})_2Cl$ (0.7, 1.75)[g]
1.24 (4.0)	*neo*-PentNC (2.0)	CH_2Cl_2 (75)	25	24	$C_3H_5Mo(CO)(neo\text{-PentNC})_3Cl$ (0.8, 1.75)[h]
0.62 (2.0)	*c*-HexNC (2.0)	CH_2Cl_2 (40)	25	~0.1	$C_3H_5Mo(CO)_2(c\text{-HexNC})_2Cl$ (0.72, 1.65)[c]
0.62 (2.0)	*c*-HexNC (2.0)	THF (60)	67		Decomposition

[a] Me = methyl; Et = ethyl; *i*-Pr = isopropyl; *t*-Bu = *tert*-butyl; *neo*-Pent = neopentyl; *c*-Hex = cyclohexyl. [b] THF = tetrahydrofuran; MCH = methylcyclohexane. [c] These compounds were purified by crystallization from mixtures of dichloromethane and hexane. [d] Solvent was removed at ~ 25° (35 mm). A concentrated solution of the residue in dichloromethane was chromatographed on a 2 × 50 cm Florisil column. The light yellow band of *cis*-$(MeNC)_4Mo(CO)_2$ was eluted with a 9:1 mixture of dichloromethane and tetrahydrofuran. Pure product was obtained by evaporation of the eluate at ~ 25° (35 mm) followed by recrystallization from a mixture of dichloromethane and hexane. The chromatography could also be carried out on an alumina column, but the compound was much more difficult to elute from the alumina column. [e] Solvent was removed from the filtered reaction mixture at ~ 25° (35 mm) to give an orange oil, shown by infrared spectroscopy to contain the $C_3H_5Mo(CO)_2(RNC)_2Cl$ derivative. [f] This product was not obtained pure and thus could not be unequivocally characterized (see text). [g] The reaction mixture was treated with 100 ml of hexane and filtered, and the filtrate was concentrated to give 1.47 g of impure product. This product was purified by chromatography on Florisil in hexane using dichloromethane containing 1–5% of acetone to elute the product followed by recrystallization from a mixture of dichloromethane and hexane. [h] This product was purified by chromatography on Florisil in hexane. A 3:1 mixture of dichloromethane and methanol was necessary to elute this product from the column. The analytical sample was also recrystallized from a mixture of dichloromethane and hexane.

ever, this reaction was found to lead first to displacement of the two acetonitrile ligands, then to stepwise replacement of the two carbonyl groups, and finally to displacement of the allyl group with retention of the chloride ligand. This reaction thus was not at all useful for the preparation of the octahedral *tert*-butyl isocyanide metal carbonyls for the spectroscopic study.[4] However, the unusual final product $[(Me_3CNC)_4MoCl]_2$ suggested a more extensive investigation of the reactions of different isocyanides with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$. An interesting feature of this work is the strong dependence of the final product from the reaction of alkyl isocyanides with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ on the specific isocyanide employed: of the six alkyl isocyanides used in this work only *tert*-butyl isocyanide gave a product of the type $[(RNC)_4MoCl]_2$ and methyl and ethyl isocyanides unlike *tert*-butyl isocyanide resulted in the reductive elimination of allyl chloride to give products of the type *cis*-$(RNC)_4Mo(CO)_2$ ($R = CH_3, C_2H_5$).

Experimental Section

The isocyanides RNC were prepared by dehydration of the corresponding formamides RNHCNO in quinoline with phosphorus oxychloride (R = cyclohexyl)[8] or *p*-toluenesulfonyl chloride (R = methyl, ethyl, isopropyl, *tert*-butyl, neopentyl).[9] They were handled in the hood because of their foul odors and toxicity. The odors of the primary alkyl isocyanides seemed far more obnoxious and repulsive than the odor of *tert*-butyl isocyanide.

The complex $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ was prepared from $Mo(CO)_6$, allyl chloride, and acetonitrile according to the published procedure.[7]

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions; (b) handling all filtered solutions of organometallic compounds; and (c) filling evacuated vessels containing organometallic compounds.

General Procedures for the Reactions of $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ with the Alkyl Isocyanides (Table I). The indicated quantities (Table I) of $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$, the alkyl isocyanide, and solvent were boiled under reflux for the indicated period of time. The procedures for the isolation of the product varied but in general followed one of the following three methods: (a) the compounds *cis*-$(RNC)_4Mo(CO)_2$ ($R = CH_3, C_2H_5$) were isolated by chromatography of a concentrated dichloromethane solution of the residue remaining after removal of the solvent at 25° (35 mm); (b) the other compounds isolated from reactions conducted in saturated hydrocarbon solvents (*i.e.*, hexane or methylcyclohexane) precipitated upon cooling the reaction mixture and were recrystallized from mixtures of dichloromethane and hexane; (c) the other compounds isolated from reactions conducted in dichloromethane were isolated by addition of hexane and concentration at 25° (35 mm). Further details of product isolation are given as footnotes to Table I.

Analytical data on the new compounds are given in Table II. Infrared and proton nmr spectroscopic data are given in Tables III and IV, respectively.

Discussion

All of the alkyl isocyanides reacted rapidly with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ at room temperature with replacement of both acetonitrile ligands by the alkyl isocyanide to give compounds of the type $C_3H_5Mo(CO)_2(RNC)_2Cl$ analogous to previously reported reactions of other ligands[5] such as 2,2′-bipyridyl and 1,2-bis(diphenylphosphino)ethane with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$. The compounds $C_3H_5Mo(CO)_2(RNC)_2Cl$ derived from methyl, *tert*-butyl, neopentyl, and cyclohexyl isocyanides were isolated in the pure solid state whereas the corresponding ethyl and isopropyl derivatives were obtained only as impure viscous liquids identified by their infrared ν(CO) and ν(CN) frequencies.

The complexes $C_3H_5Mo(CO)_2(RNC)_2Cl$ exhibit two infrared ν(CO) absorptions separated by ~85 cm^{-1} as well as two ν(CN) absorptions separated by ~10 cm^{-1} (Table III) in accord with cis arrangements of the pairs of both the carbonyl and alkyl isocyanide ligands. The smaller separation of the two ν(CN) absorptions relative to the two ν(CO) absorptions in these complexes agrees with the previously observed[4] smaller stretch–stretch interaction constant

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[8] I. Ugi and R. Meyr, *Chem. Ber.*, 93, 239 (1960).

[9] R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Syn.*, 46, 75 (1966).

Table II. Properties of the Compounds from $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and Various Isocyanides

			Analyses,[c] %							
			C		H		N		Other	
Compd[a]	Color	Mp or dec pt,[b] °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_3H_5Mo(CO)_2$(MeNC)$_2$Cl	Yellow to yellow-brown	Dec pt >105	34.8	34.5	3.6	4.3	9.0	9.6	10.3 (O)	11.5 (O)
$C_3H_5Mo(CO)_2$(*t*-BuNC)$_2$Cl	Orange	91	45.6	45.7	5.8	5.9	7.1	7.5	8.1 (O)	8.6 (O)
$C_3H_5Mo(CO)_2$(*neo*-PentNC)$_2$Cl	Yellow-orange	93–94	48.3	48.7	6.4	6.1	6.6	6.6	7.6 (O)	8.4 (O)
$C_3H_5Mo(CO)_2$(*c*-HexNC)$_2$Cl	Yellow-orange	82–83	51.1	51.5	6.1	6.4	6.3	6.4		
$C_3H_5Mo(CO)$(*t*-BuNC)$_3$Cl	Red-orange	141–142 dec	50.7	50.4	7.1	6.9	9.4	9.3	3.6 (O)	5.2 (O)
$C_3H_5Mo(CO)$(*neo*-PentNC)$_3$Cl	Yellow	105–106 dec	53.7	55.3	7.8	8.0	8.5	9.0	3.3 (O)	4.3 (O)
[(*t*-BuNC)$_4$MoCl]$_2$[d]	Yellow	161	51.8	51.1	7.8	7.8	12.1	12.4	7.7 (Cl)	8.7 (Cl)
cis-(MeNC)$_4$Mo(CO)$_2$	Light yellow	Dec pt 185	38.0	37.8	3.8	3.8	17.7	17.9	10.1 (O)	10.6 (O)
cis-(EtNC)$_4$Mo(CO)$_2$	Light yellow	Dec pt >165	45.2	45.3	5.4	5.5	15.0	15.2		

[a] See footnote *a* of Table I for abbreviations. [b] Melting and decomposition points were determined in capillaries and are uncorrected. [c] Analyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga.; Pascher Mikroanalytisches Laboratorium, Bonn, Germany; and the microanalytical laboratory of the University of Georgia under the supervision of Mr. W. Swanson. [d] Molecular weight: calcd for dimer, 928; found, 807 ($CHCl_3$), 436 and 394 (acetone).

Table III. Infrared Spectra of the Compounds from $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and Various Isocyanides[a]

Compd[b]	ν(CN) of isocyanide ligands, cm^{-1}	ν(CO) of carbonyl ligands, cm^{-1}
$C_3H_5Mo(CO)_2$(MeNC)$_2$Cl	2222 s, 2214 sh	1961 s, 1875 s
$C_3H_5Mo(CO)_2$(EtNC)$_2$Cl	2214 s, 2195 sh	1960 s, 1875 s
$C_3H_5Mo(CO)_2$(*i*-PrNC)$_2$Cl	2201 s, 2191 sh	1960 s, 1876 s
$C_3H_5Mo(CO)_2$(*t*-BuNC)$_2$Cl	2192 s, 2182 sh	1958 s, 1873 s
$C_3H_5Mo(CO)_2$(*neo*-PentNC)$_2$Cl	2208 s, 2199 sh	1961 s, 1877 s
$C_3H_5Mo(CO)_2$(*c*-HexNC)$_2$Cl	2198 s, 2188 sh	1960 s, 1874 s
$C_3H_5Mo(CO)$(*t*-BuNC)$_3$Cl	2178 m, 2129 s	1831 s
$C_3H_5Mo(CO)$(*neo*-PentNC)$_3$Cl	2201 m, 2158 s	1905 s
[(*t*-BuNC)$_4$MoCl]$_2$	2146 s, 2123 sh	
cis-(MeNC)$_4$Mo(CO)$_2$	2173 m, 2115 m, 2083 s	1870 s, 1820 s
cis-(EtNC)$_4$Mo(CO)$_2$	2161 m, 2120 sh, 2095 sh, 2071 s	1872 s, 1821 s
cis-(*t*-BuNC)$_4$Mo(CO)$_2$[c]	2140 m, 2092 m, 2055 sh, 2025 s	1864 s, 1818 s

[a] These infrared spectra were taken in CH_2Cl_2 solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. [b] See footnote *a* of Table I for abbreviations. [c] Data from R.B. King and M. S. Saran, *Inorg. Chem.*, **13**, 74 (1974).

Table IV. Proton Nmr Spectra of the Compounds from $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and Various Isocyanides[a]

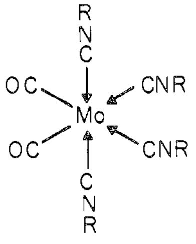
	τ,[c] ppm		
	Trihaptoallyl group		
Compd[b]	CH	CH_2	Isocyanide ligand[d]
$C_3H_5Mo(CO)_2$(MeNC)$_2$Cl	~5.3 br	~6.5,[e] 8.17 d (10)	6.48 s [CH_3]
$C_3H_5Mo(CO)_2$(*t*-BuNC)$_2$Cl	~5.4 br	6.52 d (7), 8.24 d (10)	8.47 s [CH_3]
$C_3H_5Mo(CO)_2$(*neo*-PentNC)$_2$Cl	~5.3 br	6.47 d (6), 8.17 d (11)	6.61 s [CH_2], 8.90 s [CH_3]
$C_3H_5Mo(CO)_2$(*c*-HexNC)$_2$Cl	~5.4 br	6.49 d (7), *f*	6.09 br [CH], 8.13, 8.53 [CH_2]
$C_3H_5Mo(CO)$(*t*-BuNC)$_3$Cl	~5.3 br	6.45 d (7), 7.88 d (11)	8.42 s, 8.51 s [CH_3: rel intens ~1:2]
$C_3H_5Mo(CO)$(*neo*-PentNC)$_3$Cl	*g*	6.69 d (7), 7.41 d (11)	6.44 s [CH_2], 8.91 s [CH_3]
[(*t*-BuNC)$_4$MoCl]$_2$			8.43 s [CH_3]
cis-(MeNC)$_4$Mo(CO)$_2$			6.67 s [CH_3]
cis-(EtNC)$_4$Mo(CO)$_2$			6.43 q (7) [CH_2], 8.63 t (7), 8.66 t (7) [CH_3: rel intens ~1:1]

[a] These spectra were taken in $CDCl_3$ solutions and recorded at 100 MHz on a Varian HA-100 spectrometer. [b] See footnote *a* of Table I for abbreviations. [c] s = singlet, d = doublet, t = triplet, q = quartet, br = broad; coupling constants in hertz are given in parentheses. [d] The assignments are given in brackets. [e] This resonance was partially obscured by the methyl isocyanide resonance. [f] This resonance was completely obscured by the strong cyclohexyl resonance. [g] The signal-to-noise ratio did not allow unambiguous detection of this resonance.

parameters for the *tert*-butyl isocyanide derivatives of the octahedral metal carbonyls. The ν(CO) absorptions (1960 ± 2 and 1875 ± 2 cm^{-1}) are essentially insensitive to the alkyl group of the isocyanide whereas the positions of the isocyanide ν(CN) absorptions decrease systematically in successive ~10-cm^{-1} increments from methyl through primary alkyl (ethyl or neopentyl) and secondary alkyl (isopropyl or cyclohexyl) to *tert*-butyl. The proton nmr spectra of all of the $C_3H_5Mo(CO)_2(RNC)_2Cl$ complexes isolated in the pure state exhibit nearly identical resonances for the protons of the alkyl group (Table IV) as well as the expected resonances for the protons of the isocyanide ligand.

The course of the further reactions of the $C_3H_5Mo(CO)_2(RNC)_2Cl$ complexes with more alkyl isocyanide under vigorous conditions depends upon the alkyl isocyanide. In some cases (isopropyl and cyclohexyl isocyanides) polymerization of the isocyanide as well as decomposition prevents the isolation in the pure state of any products from such further reactions. Methyl and ethyl isocyanides ultimately form the corresponding *cis*-$(RNC)_4Mo(CO)_2$ (I, R = CH_3, C_2H_5) complexes upon reaction with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$. The complexes *cis*-$(RNC)_4Mo(CO)_2$ (I, R = CH_3, C_2H_5) exhibit very similar $\nu(CO)$ frequencies to those of the previously reported[4] analogous *tert*-butyl isocyanide complex but the $\nu(CN)$ frequencies are shifted as in the corresponding $C_3H_5Mo(CO)_2(RNC)_2Cl$ complexes discussed above (Table III).

A curious effect was observed in the proton nmr spectra of complexes of the type *cis*-$(RNC)_4Mo(CO)_2$ (I), where the alkyl isocyanide ligands form two nonequivalent pairs: those trans to each other and those trans to a carbonyl group. The proton nmr spectrum of the *tert*-butyl isocyanide complex *cis*-$(Me_3CNC)_4Mo(CO)_2$ (I, R = *tert*-butyl) was previously[4] found to exhibit two *tert*-butyl resonances of equal intensities corresponding to the two nonequivalent pairs of *tert*-butyl isocyanide ligands. However, the proton nmr spectrum of *cis*-$(CH_3NC)_4Mo(CO)_2$ (I, R = methyl) exhibits only a single methyl resonance (Table IV) despite the two nonequivalent pairs of methyl isocyanide ligands required by structure I. The proton nmr spectrum of the corresponding ethyl isocyanide complex *cis*-$(C_2H_5NC)_4Mo(CO)_2$ clarified this mystery by exhibiting a single quartet CH_2 resonance but two closely spaced triplet CH_3 resonances of equal relative intensities. These observations indicate that in alkyl isocyanide complexes, at least those of the type *cis*-$(RNC)_4Mo(CO)_2$ (I), the chemical shifts of protons on the β-carbon atom of the alkyl isocyanide are more sensitive to changes in the environment of the isocyanide ligand than those of the protons on the α-carbon atom.



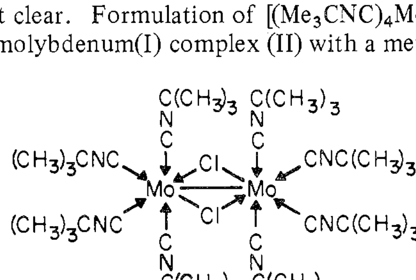
I

Further reaction of *tert*-butyl isocyanide with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ under more vigorous conditions does not result in displacement of allyl chloride to form *cis*-$(Me_3CNC)_4Mo(CO)_2$ but instead in replacement of an additional carbonyl group to form $C_3H_5Mo(CO)(Me_3CNC)_3Cl$. The ultimate identifiable reaction product from *tert*-butyl isocyanide and $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ is an allyl-free and carbonyl-free derivative of stoichiometry $[(Me_3CNC)_4MoCl]_2$. Under conditions intermediate between those suitable for formation of $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ and those suitable for formation of $[(Me_3CNC)_4MoCl]_2$ (*e.g.*, in boiling tetrahydrofuran or hexane) the reaction gave an orange solid characterized by allyl nmr resonances at τ 5.31 (multiplet), τ 6.95 (doublet, $J = 7$ Hz), and τ 7.79 (doublet, $J = 12$ Hz), *tert*-butyl isocyanide $\nu(CN)$ frequencies at 2141 (m), 2113 (s), and 2051 (s) cm^{-1}, and the absence of metal carbonyl $\nu(CO)$ frequencies. This product analyzed approximately for $C_3H_5Mo(Me_3CNC)_4Cl$. (*Anal.* Calcd for this formula: C, 54.7; H, 8.1; N, 11.1; Cl, 7.0. Found: C, 55.1; H, 8.6; N, 11.9; Cl, 6.1.) However, this compound could never be obtained free spectroscopically (infrared and proton nmr) from either $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ or $[(Me_3CNC)_4MoCl]_2$ since reaction conditions could not be found which formed the presumed $C_3H_5Mo(Me_3CNC)_4Cl$ free from one of the other two complexes. Furthermore, attempts to purify the presumed $C_3H_5Mo(Me_3CNC)_4Cl$ by chromatography led to extensive decomposition and incomplete separation.

The compound $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ obtained from extended room-temperature reaction of *tert*-butyl isocyanide with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ exhibits the expected single infrared $\nu(CO)$ frequency in addition to two infrared alkyl isocyanide $\nu(CN)$ frequencies (Table III). The proton nmr spectrum of $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ (Table IV) besides confirming the presence of the allyl group also indicates two types of *tert*-butyl isocyanide ligands in a 2:1 ratio consistent with the fact the only one of the three *tert*-butyl isocyanide ligands can be trans to a carbonyl group.

Extended reaction of neopentyl isocyanide with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ at room temperature also gave a monocarbonyl $C_3H_5Mo(CO)(Me_3CCH_2NC)_3Cl$, but attempts to force this reaction further to a carbonyl-free and/or allyl-free neopentyl isocyanide complex failed owing to complete decomposition and apparent polymerization of the neopentyl isocyanide. The positions of the allyl proton nmr resonances and the single infrared $\nu(CO)$ frequencies in the two complexes $C_3H_5Mo(CO)(RNC)_3Cl$ (R = *tert*-butyl or neopentyl) are very different (Table III) suggesting them to have different stereochemical arrangements of the ligands around the molybdenum atom. The proton nmr resonances of the protons on both the α- and γ-carbon atoms of the neopentyl isocyanide ligands in $C_3H_5Mo(CO)(Me_3CNC)_3Cl$ (Table IV) fail to indicate any nonequivalence of the three neopentyl isocyanide ligands in this complex. This probably reflects the lower sensitivity to small changes in the environment of the alkyl isocyanide ligand of the nmr resonances of protons on the α- and γ-carbon atoms relative to the protons on the β-carbon atoms such as found for the complexes *cis*-$(RNC)_4Mo(CO)_2$ discussed above.

The final product from the reaction of *tert*-butyl isocyanide with $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ is the complex $[(Me_3CNC)_4MoCl]_2$. The diamagnetism and approximate equivalence of the *tert*-butyl isocyanide ligands in this complex are indicated by a single sharp *tert*-butyl isocyanide proton nmr resonance in the normal region. This *tert*-butyl isocyanide proton resonance remained unchanged upon cooling to −46° in $(CD_3)_2CO$ solution. Neither the proton nmr spectrum up to τ 40 in $(CD_3)_2CO$ nor the infrared spectrum around 2000 cm^{-1} provides any indication of "extra" hydrogen atoms as Mo–H units. These observations indicate that this complex is not monometallic. The molecular weight determination in the noncoordinating chloroform suggests the indicated bimetallic formulation, but molecular weight determinations in the coordinating acetone give values corresponding to the otherwise impossible monometallic formulation for reasons that are not clear. Formulation of $[(Me_3CNC)_4MoCl]_2$ as a bimetallic molybdenum(I) complex (II) with a metal–metal bond and bridging chlorine atoms gives each molybdenum atom the favored rare gas electronic configuration and can



II

account for all of the experimental observations if some tendency for dissociation of isocyanide ligands in coordinating solvents is assumed in order to rationalize the low molecular weight determinations in methyl ethyl ketone. The single resonance for the *tert*-butyl isocyanide protons can arise from stereochemical nonrigidity of the seven-coordinate molybdenum(I) atom or the rapid reversible dissociation of the *tert*-butyl isocyanide ligands.

In an attempt to prepare a cyclopentadienylmolybdenum-*tert*-butyl isocyanide derivative related to those studied in the previous paper[1] the reaction of $[(Me_3CNC)_4MoCl]_2$ with sodium cyclopentadienide in boiling tetrahydrofuran was investigated. However, this reaction gave an intractable product.

The reactions between various alkyl isocyanides and $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ provide an unusual example of a system where the choice of the alkyl isocyanide can greatly affect the type of metal complex formed. The reaction between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and methyl isocyanide to replace allyl chloride forming *cis*-$(CH_3NC)_4Mo(CO)_2$ after removal of the acetonitrile ligands contrasts significantly with the reaction between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and *tert*-butyl isocyanide to replace the carbonyl groups and finally the allyl group with retention of the chlorine to form $[(Me_3CNC)_4MoCl]_2$. The sensitivity of the reactions between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and alkyl isocyanides to changes in the alkyl isocyanide as compared with the reported reactions[10] between other transition metal complexes and alkyl isocyanides can be a consequence of the four different types of ligands in $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ which are potentially replaceable by alkyl isocyanides. Transition metal complexes previously used for reactions with alkyl and aryl isocyanides have not contained such a variety of different ligands as $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$.

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Registry No. $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$, 33221-75-9; $C_3H_5Mo(CO)_2(MeNC)_2Cl$, 51933-93-8; $C_3H_5Mo(CO)_2(EtNC)_2Cl$, 51933-94-9; $C_3H_5Mo(CO)_2$(*i*-PrNC)$_2$Cl, 51933-95-0; $C_3H_5Mo(CO)_2$(*t*-BuNC)$_2$Cl, 51933-96-1; $C_3H_5Mo(CO)_2$(*neo*-PentNC)$_2$Cl, 51933-97-2; $C_3H_5Mo(CO)_2$(*c*-HexNC)$_2$Cl, 51933-98-3; $C_3H_5Mo(CO)$(*t*-BuNC)$_3$Cl, 51933-99-4; $C_3H_5Mo(CO)$(*neo*-PentNC)$_3$Cl, 52022-17-0; [(*t*-BuNC)$_4$MoCl]$_2$, 52022-18-1; *cis*-(MeNC)$_4$Mo(CO)$_2$, 51933-82-5; *cis*-(EtNC)$_4$Mo(CO)$_2$, 51933-83-6.

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[10] (a) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, London, 1969; (b) P. M. Treichel, *Advan. Organometal. Chem.*, 11, 21 (1973).

Contribution from the McPherson Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Stereochemical Studies at Pseudotetrahedral, Chiral Metal of the Decarbonylation, Carbonylation, and Sulfur Dioxide Insertion Reactions

PETER REICH-ROHRWIG and ANDREW WOJCICKI*

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The stereochemistry of insertion and elimination reactions at the metal center in pseudotetrahedral, chiral organoiron complexes was investigated by ^1H nmr spectroscopy. The acyl complex η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ was synthesized by treatment of η^5-$C_5H_5Fe(CO)_2CH_2CH(CH_3)C_6H_5$ with $P(C_6H_5)_3$ and was separated into two diastereomerically related pairs of enantiomers by a combination of column chromatography and crystallization from benzene–pentane. The photochemical decarbonylation of each pair of enantiomers of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ in benzene solution proceeds with high stereospecificity (>64% retention or inversion) but is complicated by unequal stabilities of the isomers of the alkyl product η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$. The carbonylation of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ in acetonitrile at 25° and under 4 atm of CO provided no stereochemical information on the reaction owing to configurational instability of the starting alkyl complex under these conditions. By contrast, the SO_2 insertion reaction of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ in neat SO_2 or in a *ca.* 2 *M* solution of SO_2 in CH_2Cl_2 takes place with high stereospecificity (⩾90% retention or inversion) to yield η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_2CH(CH_3)C_6H_5$. The implications of these results to the mechanism of the respective reactions are considered and discussed.

Introduction

Organometallic insertion and elimination reactions at transition metal-carbon σ bonds have attracted considerable interest in recent years.[1-3] This is largely attributable to their occurrence in a number of important stoichiometric and catalytic processes, *e.g.*, hydroformylation and polymerization.[4-6]

In this context, much attention has focused on the mechanism. Kinetic studies have been carried out on the carbonylation,[2] decarbonylation,[2] and sulfur dioxide insertion[3,7] in several different types of complexes containing transition metal-carbon σ bonds. Stereochemical investigations have established that the mechanism of the carbonylation and the decarbonylation is consistent with migration of the alkyl group onto the nearest coordination site of the metal.[2,8] For the SO_2 insertion, gross stereochemistry was found to be preserved in the formation of *cis*-$Mn(CO)_4[P(C_6H_5)_3]S(O)_2$-

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[1] M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, 5, 225 (1967).

[2] A. Wojcicki, *Advan. Organometal. Chem.*, 11, 87 (1973).

[3] A. Wojcicki, *Advan. Organometal. Chem.*, 12, 31 (1974).

[4] R. F. Heck, *Accounts Chem. Res.*, 2, 10 (1969).

[5] M. Orchin and W. Rupilius, *Catal. Rev.*, 6, 85 (1972).

[6] J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969).

[7] S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, 95, 6962 (1973).

[8] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, 10, 101 (1967).