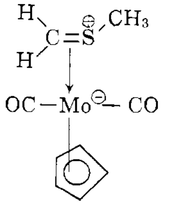
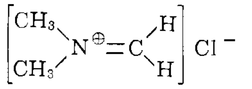
strongly adsorbed orange cyclic acyl derivative was observed during the chromatography of one preparation of $NC_5H_4CH_2Fe(CO)_2C_5H_5$. Finally, $NaW(CO)_3C_5H_5$, which does not form a cyclic acyl derivative with 2-chloromethylpyridine, reacts with acyl halides to form acyl derivatives of the type $RCOW(CO)_3C_5H_5$ which could be decarbonylated neither on heating below the decomposition temperature nor on irradiation at room temperature or slightly above.



IX



X

In our studies on organosulfur derivatives of metal carbonyls we investigated reactions between chloromethyl methyl sulfide and metal carbonyl anions.[2,3] These studies resulted in the discovery of unusual compounds such as $CH_3SCH_2Mo(CO)_2C_5H_5$ (IX) for which structures with a carbon–sulfur double bond π-bonded to a metal atom were proposed. Somewhat analogous to chloromethyl methyl sulfide is chloromethyldimethylamine. A material of composition $(CH_3)_2NCH_2Cl$ is known.[24] However, this material is an ionic nonvolatile solid in contrast to the volatile liquid CH_3SCH_2Cl and has the structure X containing a cation with a carbon–nitrogen double bond. A sample of this material was prepared and allowed to react with tetrahydrofuran solutions of the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$. However, in both cases the corresponding coupling products $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Mo(CO)_3]_2$, respectively, instead of any $(CH_3)_2NCH_2$ metal complexes were the major metal carbonyl products obtained from these reactions. In the case of the reaction between $NaFe(CO)_2C_5H_5$ and $(CH_3)_2NCH_2Cl$ a small quantity of an unstable brown liquid possibly containing some $(CH_3)_2NCH_2Fe(CO)_2C_5H_5$ was observed; this was not studied in detail.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this research under Grant No. AF-AFOSR-580-64. We are grateful to A. Fronzaglia for experimental assistance.

[24] H. Böhme, W. Lehners, and G. Keitzer, *Ber.*, **91**, 340 (1958).

Contribution from the Mellon Institute,
Pittsburgh, Pennsylvania

Organonitrogen Derivatives of Metal Carbonyls. II. Arylazo Derivatives of Molybdenum[1,2]

By R. B. King and M. B. Bisnette

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Aryldiazonium tetrafluoroborates or hexafluorophosphates react with $NaMo(CO)_3C_5H_5$ in tetrahydrofuran solution to form the red compounds $RN_2Mo(CO)_2C_5H_5$ (R = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$O_2NC_6H_4$, and 1-$C_{14}H_7O_2N_2$). The p-tolyl derivative p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ reacts with triphenylphosphine or dimethyl disulfide with loss of metal carbonyl groups but preservation of the arylazo ligand to give red $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ or brown $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$, respectively.

Formally low oxidation states of transition metals were first encountered in the metal carbonyls[3] and metal nitrosyls[4] over 75 years ago. Derivatives of these CO and NO^+ ligands[5] have frequently played an important role in the subsequent development of coordination chemistry. About 15 years ago the analogy between the carbonyl and aryl isocyanide groups was recognized[6] leading to the preparation of numerous RNC complexes analogous to well-established metal carbonyls.[7] Although aryl isocyanides did not stabilize extremely low oxidation states to the large extent of carbon monoxide,[8] stable zerovalent isocyanide derivatives such as $Cr(CNR)_6$ could be readily prepared.

The aryl isocyanide ligand, RNC, may be considered

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[1] For Part I of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 293 (1966).

[2] For a preliminary communication of some of this work see R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 5694 (1964).

[3] The first known metal carbonyl was $Ni(CO)_4$. See L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, **57**, 749 (1890).

[4] Probably the first known metal nitrosyls were the nitroprussides $M_2[Fe(CN)_5NO]$ prepared by Playfair in 1849. See N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford, London, 1950, pp. 1343–1346.

[5] The formal charge on ligands, especially those with strongly partial double bonding tendencies such as CO, NO, and C_nH_n (n = 4, 5, 6, 7, etc.), in transition metal complexes is often unclear. In particular, it is convenient to regard formally the nitrosyl ligand as NO^+ for development of the analogy between related transition metal nitrosyl and arylazo derivatives. We realize, of course, that in many metal nitrosyl derivatives the charge on the nitrosyl ligand will more closely approach NO^-; such compounds, however, may be regarded as NO^+ complexes where the nitrosyl group acquires a net negative charge by accepting electron density from the filled d orbitals of the transition metal atoms by means of partial metal–nitrogen double bonding. A similar effect is likely to occur in the arylazo compounds discussed in this paper.

[6] W. Hieber, *Z. Naturforsch.*, **5b**, 129 (1950).

[7] For a review of isocyanide complexes of metals see L. Malatesta, *Progr. Inorg. Chem.*, **1**, 284 (1959).

[8] For example, isocyanide analogs of the metal carbonyl anions with the metal in a negative oxidation state are unknown.

as related to carbon monoxide, CO, by replacement of an oxygen atom with an arylimino group, RN. Analogous replacement of the oxygen atom in the NO$^+$ ligand with an arylimino group leads to the RNN$^+$ or RN$_2$$^+$ ligand. The free RN$_2$$^+$ ligand is, of course, the cation in the long-known, well-established, and technically important diazonium salts.[9] Closely-related covalent derivatives are the arylazo compounds such as azobenzene.[10] However, no arylazo derivatives of transition metals analogous to metal nitrosyls had been reported when we started experimental work in this area in 1964. However, since the original communication[2] of our preliminary results, Parshall[11] has reported some arylazo derivatives of platinum. Parshall's studies have involved systems very different from our studies. His compounds, although apparently containing the same RN$_2$$^+$ ligand as our compounds, also differ from our compounds by neither corresponding to known metal nitrosyl derivatives nor containing metal carbonyl groups.

This paper describes the preparation and properties of several arylazo compounds of molybdenum of the type RN$_2$Mo(CO)$_2$C$_5$H$_5$. Furthermore chemical studies on the *p*-tolyl derivatives *p*-CH$_3$C$_6$H$_4$N$_2$Mo(CO)$_2$C$_5$H$_5$ (the more straightforward of which are described in this paper) coupled with various miscellaneous information suggest reasons discussed below for the relatively late discovery and limited scope of the arylazo–transition metal compounds.

Experimental Section

Microanalyses (*e.g.*, Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.[12] Molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., with the Mechrolab vapor pressure osmometer using benzene solutions. In general infrared spectra (Table II) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl regions of many compounds (Table II) were taken in either dilute cyclohexane solution or a halocarbon oil mull and recorded on a Beckman IR-9 spectrometer with grating optics and using an expanded scale (expansion factor 2.5 or 4). Ultraviolet spectra were taken in cyclohexane solution and recorded on a Cary Model 14 spectrometer. Proton n.m.r. spectra (Table III) were taken in carbon disulfide solution (unless otherwise indicated) and recorded on a Varian A-60 spectrometer.

Tetrahydrofuran was distilled over lithium aluminum hydride immediately before use. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with organometallic compounds, (b) admitting to evacuated flasks and other vessels, and (c) handling filtered solutions of organometallic compounds. Chromatographic separations were carried out on 80–200 mesh adsorption alumina (Fisher Scientific Co., No. A-540).

Hexacarbonylmolybdenum was purchased from the Climax Molybdenum Co., New York, N. Y. Heating Mo(CO)$_6$ with dicyclopentadiene according to published procedures[13] gave [C$_5$H$_5$Mo(CO)$_3$]$_2$. The sodium salt NaMo(CO)$_3$C$_5$H$_5$ was prepared either from [C$_5$H$_5$Mo(CO)$_3$]$_2$ and a 30% excess of dilute sodium amalgam in tetrahydrofuran at room temperature[14] or from hexacarbonylmolybdenum and a 20% excess of sodium cyclopentadienide in tetrahydrofuran at its boiling point.[15]

The aromatic amines used to prepare the diazonium salts were commercial samples from usual sources used without special purification.

Preparation of Solid Aryldiazonium Salts.[16]—Aniline, *p*-anisidine, *p*-toluidine, *p*-phenylenediamine, and *p*-nitroaniline were diazotized by the usual procedure by addition of sodium nitrite to an ice-cooled solution of the amine in dilute aqueous hydrochloric acid. The tetrafluoroborate or hexafluorophosphate salt was then precipitated from the resulting solution by addition of excess 47% aqueous tetrafluoroboric acid or 65% aqueous hexafluorophosphoric acid, respectively.

1-Aminoanthraquinone is a weaker base than the other amines used.[17] Conversion of this amine to the corresponding diazonium salt was carried out in concentrated sulfuric acid followed by the usual precipitation of the tetrafluoroborate by addition of excess 47% tetrafluoroboric acid.

The nature of some of these salts was checked by elemental analyses: (1) [*p*-CH$_3$C$_6$H$_4$N$_2$][BF$_4$]: Calcd. for C$_7$H$_7$BF$_4$N$_2$: C, 40.8; H, 3.4; N, 13.6. Found: C, 41.2; H, 3.3; N, 14.0. (2) [*p*-CH$_3$OC$_6$H$_4$N$_2$][BF$_4$]: Calcd. for C$_7$H$_7$BF$_4$N$_2$O: C, 37.9; H, 3.2; N, 12.6. Found: C, 37.6; H, 3.0; N, 12.9. (3) [*p*-O$_2$NC$_6$H$_4$N$_2$][BF$_4$]: Calcd. for C$_6$H$_4$BF$_4$N$_3$O$_2$: C, 30.4; H, 1.7; N, 17.7. Found: C, 30.2; H, 1.8; N, 18.0. (4) [1-C$_{14}$H$_7$O$_2$N$_2$][BF$_4$]: Calcd. for C$_{14}$H$_7$BF$_4$N$_2$O$_2$: C, 52.2; H, 2.4; N, 8.7. Found: C, 52.3; H, 2.4; N, 8.7. (5) [*p*-C$_6$H$_4$(N$_2$)$_2$][BF$_4$]$_2$: Calcd. for C$_6$H$_4$B$_2$F$_8$N$_4$: C, 23.6; H, 1.3; N, 18.3. Found: C, 23.5: H, 1.6; N, 18.1.

General Procedure for the Preparation of RN$_2$Mo(CO)$_2$C$_5$H$_5$ Compounds.—The procedure described below was used for the preparation of the three compounds C$_6$H$_5$N$_2$Mo(CO)$_2$C$_5$H$_5$, *p*-CH$_3$C$_6$H$_4$N$_2$Mo(CO)$_2$C$_5$H$_5$, and *p*-CH$_3$OC$_6$H$_4$N$_2$Mo(CO)$_2$C$_5$H$_5$. Many as yet unprepared related RN$_2$Mo(CO)$_2$C$_5$H$_5$ compounds where R is a benzene ring containing only relatively inert functional groups such as alkyl and alkoxy should also be preparable by this same procedure.

A solution of 22.5 mmoles of NaMo(CO)$_3$C$_5$H$_5$ in 100 ml. of tetrahydrofuran was prepared from [C$_5$H$_5$Mo(CO)$_3$]$_2$ and sodium amalgam.[14] It was then treated gradually *in portions*[18] with 15 mmoles of the solid aryldiazonium salt. The reaction mixture became red with gas evolution. After stirring overnight (~16 hr.) at room temperature solvent was removed at ~25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane solution at ~25° (30 mm.). A filtered extract of the residue in ~50 ml. of diethyl ether was chromatographed

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[9] For detailed discussions on the chemistry of the diazonium salts see K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," Longmans, Green, and Co., New York, N. Y., 1949, and H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

[10] Since the new molybdenum derivatives discussed in this paper have the RN$_2$$^+$ ligand *covalently* bonded to the molybdenum atom we prefer to call them arylazo rather than aryldiazonium derivatives.

[11] G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 2133 (1965).

[12] On compounds containing carbon, molybdenum, nitrogen, and phosphorus or sulfur (*e.g.*, [CH$_3$SMo(N$_2$C$_7$H$_7$)C$_5$H$_5$]$_2$) including compounds described both in this and previous papers, a persistent trend toward carbon values 1–3% low has been encountered.

[13] R. B. King, "Organometallic Syntheses," Academic Press, New York, N. Y., 1965, Vol. I, p. 109, and references cited therein.

[14] R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

[15] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[16] Since solid aryldiazonium tetrafluoroborates and hexafluorophosphates are often useful for the preparation of fluoroaromatic compounds, papers and books on fluoroaromatic compounds often give useful information on these diazonium salts. See, for example, A. Roe in "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 5, and A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1962.

[17] F. Kačer and R. Scholl, *Ber.*, **37**, 4185 (1904).

[18] If the aryldiazonium salt is added in one portion to the NaMo(CO)$_3$C$_5$H$_5$ solution at room temperature, none of the desired RN$_2$Mo(CO)$_2$C$_5$H$_5$ compound is obtained (at least in the cases of the phenyl and *p*-methoxyphenyl derivatives). Instead purple-red ether-insoluble decomposition products are obtained. Formation of the red-purple decomposition products may also be suppressed by adding the diazonium salt to the NaMo(CO)$_3$C$_5$H$_5$ solution at −78° and then warming to room temperature. This technique was not generally used for the work described in this paper but has subsequently been used to prepare the *p*-tolyl derivative *p*-CH$_3$C$_6$H$_4$N$_2$Mo(CO)$_2$C$_5$H$_5$ in 65% yield for other purposes.

TABLE I

COMPOUNDS OF THE TYPE $RN_2Mo(CO)_2C_5H_5$

Compound	Color	M.p., °C.	Reaction	Yield, %		Analyses, %					Mol. wt.
						C	H	N	O	Mo	
(1) $C_6H_5N_2Mo(CO)_2C_5H_5$	Dark red	41–43	$NaMo(CO)_3C_5H_5$ + $[C_6H_5N_2][PF_6]$	25	Calcd.	48.5	3.1	8.7	9.9	29.8	
					Found	48.1	2.6	8.3	10.4	30.8	
			$NaMo(CO)_3C_5H_5$ + $[p\text{-}C_6H_4(N_2)_2][BF_4]_2$	6							
(2) $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$	Red	64–66	$NaMo(CO)_3C_5H_5$ + $[p\text{-}CH_3C_6H_4N_2][BF_4]$	26–46	Calcd.	50.0	3.6	8.3	9.5	28.6	336
					Found	49.8	4.3	8.0	10.5	27.4	347
(3) $p\text{-}CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$	Red-orange	78–79	$NaMo(CO)_3C_5H_5$ + $[p\text{-}CH_3OC_6H_4N_2][BF_4]$	21	Calcd.	47.7	3.4	7.9	13.6	27.2	352
					Found	47.8	3.7	8.0	13.8	26.9	338
(4) $p\text{-}O_2NC_6H_4N_2Mo(CO)_2C_5H_5$	Green-brown	128–130	$NaMo(CO)_3C_5H_5$ + $[p\text{-}O_2NC_6H_4N_2][BF_4]$	10	Calcd.	42.5	2.4	11.4	17.4	26.2	
					Found	42.9	2.4	11.3	17.2	26.5	
(5) $C_{14}H_7O_2N_2Mo(CO)_2C_5H_5$	Red	Dec. >110°	$NaMo(CO)_3C_5H_5$ + $[C_{14}H_7O_2N_2][BF_4]$	1	Calcd.	55.8	2.7	6.2	14.2		
					Found	55.3	3.3	5.8	14.6		

TABLE II

INFRARED SPECTRA OF ARYLAZOMOLYBDENUM COMPOUNDS ($CM.^{-1}$)

Compound	ν_{CO}[a]	ν_{CH}[b,c]	Other[b]
(1) $C_6H_5N_2Mo(CO)_2C_5H_5$	2000 s, 1928 vs, 1899 w	c	1615 m, 1570 w, 1545 s, 1470 m, 1170 w, 1133 vw, 1065 vw, 1000 vw, 899 vw, 833 vw, 797 w, 747 w, 717 w
(2) $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$	1997 s, 1925 vs, 1897 w	3050 vvw	1602 s, 1585 m, sh, 1550 s, sh, 1540 s, 1488 m, 1480 w, 1434 vw, 1408 vw, 1371 vw, 1280 vw, 1202 vw, 1185 w, 1104 vw, 1095 vw, 1047 vw, 1002 w, 832 w, 810 m, 799 m, 738 w
(3) $p\text{-}CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$	1993 s, 1920 s	c	1600 s, 1570 m, 1545 m, 1490 m, 1480 sh, 1458 w, 1435 w, 1255 m, 1240 w, 1178 w, 1105 vw, 1023 vw, 1004 vw, 834 sh, 827 w, 815 vw, 801 w, 740 w
(4) $p\text{-}O_2NC_6H_4N_2Mo(CO)_2C_5H_5$	2010 s, 1942 s	3070 w	1603 m, 1586 m, 1540–1500 vvs, 1473 s, 1450 sh, 1415 sh, 1362 w, 1325 vs, 1233 vw, 1222 sh, 1190 m, 1148 s, 1102 s, 1004 w, 860 m, 846 s, 811 s, 746 s, 682 w
(5) $1\text{-}C_{14}H_7O_2N_2Mo(CO)_2C_5H_5$	1991 s, 1892 s[d]	3050 vvw	1660 m,[e] 1590 m, 1530 s, 1427 m, 1317 m, 1267 s, 1191 w, 1175 w, 1160 vw, 988 w, 909 vw, 861 w, 831 vw, 799 w, 734 w, 725 w, 703 m

[a] These ν_{CO} absorptions were observed in cyclohexane solution unless otherwise indicated. [b] These absorptions were observed in potassium bromide pellets. [c] Many of the ν_{CH} absorptions were too weak to be unequivocally identified. [d] In view of the insolubility of this compound in cyclohexane, the ν_{CO} absorptions were observed in a halocarbon oil mull. [e] This band is the ν_{CO} absorption of the carbonyl group of the anthraquinone system.

TABLE III

PROTON N.M.R. SPECTRA OF ARYLAZOMOLYBDENUM COMPOUNDS, τ

Compound	Solvent	Aryl			$\pi\text{-}C_5H_5$	CH_3	Other
		A	B	J_{AB}			
(1) $C_6H_5N_2Mo(CO)_2C_5H_5$	CS_2		2.79[a]		4.38	...	...
(2) $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$	CS_2		2.85[a]		4.34	7.63	...
(3) $p\text{-}CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$	CS_2	2.81	3.21	9	4.37	6.25	...
(4) $p\text{-}O_2NC_6H_4N_2Mo(CO)_2C_5H_5$	CS_2	1.88	2.67	9	4.24	...	...
(5) $(C_6H_5)_3PMoCO(N_2C_6H_4CH_3)C_5H_5$	$(CD_3)_2CO$		2.87[a]		4.58	7.73	2.50 $[(C_6H_5)_3P]$
	$CHCl_3$		b		4.81	7.75	b
(6) $[CH_3SMo(N_2C_6H_4CH_3)C_5H_5]_2$	CS_2	2.62	3.58	7	4.38	7.68 7.72	...

[a] Only one resonance due to all of the aryl protons was observed. [b] These resonances were hidden by the solvent resonances.

on a 2 × 50 cm. alumina column. After development with diethyl ether, the single orange band[19] of the $RN_2Mo(CO)_2C_5H_5$ compound was eluted with diethyl ether. Solvent was removed from the filtered red diethyl ether eluate at ~25° (30 mm.). The dark red product was extracted with 50–100 ml. of pentane. Cooling the filtered pentane extracts for several hours in a −78° bath precipitated red to orange crystals of the $RN_2Mo(CO)_2C_5H_5$ compound. After filtration and drying the products were obtained in the yields (generally around ~20%) and with the melting points listed in Table I.

For a more detailed study of its chemistry larger samples of the p-tolyl derivative $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ were obtained similarly by the reaction between 112.5 mmoles of $NaMo(CO)_3C_5H_5$ (prepared from $Mo(CO)_6$ and NaC_5H_5) and 15 g. (0.073 mmole) of $[p\text{-}CH_3C_6H_4N_2][BF_4]$ in 300 ml. of tetrahydrofuran. After isolation and purification by a procedure similar to that given above but using a 5 × 50 cm. alumina column and 350 ml. of boiling pentane for the final crystallization, 8.3–11.3 g. (34–46% yield) of red $p\text{-}CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ was obtained.

Preparation of $p\text{-}O_2NC_6H_4N_2Mo(CO)_2C_5H_5$.—The preparation of $p\text{-}O_2NC_6H_4N_2Mo(CO)_2C_5H_5$ was carried out slightly differently from the general procedure cited above owing to difficulty in separating the p-nitrophenylazo derivative from other products of the reaction such as $[C_5H_5Mo(CO)_3]_2$.

A solution of 50 mmoles of $NaMo(CO)_3C_5H_5$ in 300 ml. of tetrahydrofuran was prepared from $Mo(CO)_6$ and NaC_5H_5 and treated with 7.1 g. (30 mmoles) of $[p\text{-}O_2NC_6H_4N_2][BF_4]$ at −78°. The resulting deep red reaction mixture was allowed to warm slowly to room temperature and stirred for 16 hr. at room temperature. After boiling under reflux for 1 hr., the reaction mixture was cooled back to room temperature and solvent was removed at ~25° (30 mm.). The residue was extracted with four 100-ml. portions of dichloromethane. Solvent was removed

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[19] Frequently a red-purple zone consisting of decomposition products remains at the top of the column. This material is not eluted with diethyl ether.

from the filtered dichloromethane extracts at ~25° (30 mm.), leaving a red-black residue.

This residue was extracted with 250 ml. of diethyl ether in five portions. The filtered red extracts were concentrated to 150 ml. and chromatographed on a 5 × 50 cm. alumina column.[20] The chromatogram was developed with diethyl ether. A weak red-purple band (I) followed by an intense red-orange band (II) was observed. In addition, a brown band (III) remained near the top of the column. Bands I and II were eluted with diethyl ether and band III with acetone. The eluate from band I yielded only $[C_5H_5Mo(CO)_3]_2$ and the eluate from band III yielded a red-brown liquid containing no π-C_5H_5 ligands (from n.m.r.) and thus was not of particular interest. Band II contained the desired p-$O_2NC_6H_4N_2Mo(CO)_2C_5H_5$. Evaporation at 25° (30 mm.) of the filtered eluate (volume ~350 ml.) from this band left behind brown crystals. These crystals were dissolved in diethyl ether, and the filtered solution was cooled several hours at −78° to give 0.266 g. (2.4% yield) of green-brown crystalline p-$O_2NC_6H_4N_2Mo(CO)_2C_5H_5$ after filtration. Addition of hexane to the filtrate followed by slow evaporation at 30 mm. gave an additional 0.790 g. (7.2% yield) of less pure product.

Preparation of 1-$C_{14}H_7O_2N_2Mo(CO)_2C_5H_5$.—A solution of 22.5 mmoles of $NaMo(CO)_3C_5H_5$ in 100 ml. of tetrahydrofuran was treated gradually with 4.8 g. (15 mmoles) of 1-anthraquinonediazonium tetrafluoroborate. The general procedure cited above was then followed until elution of the chromatogram. In the case of this anthraquinone derivative elution with diethyl ether removed only $[C_5H_5Mo(CO)_3]_2Hg$, a yellow band, from the column. The desired product, 1-$C_{14}H_7O_2N_2Mo(CO)_2C_5H_5$, even after continued development and elution with diethyl ether remained at the top of the chromatography column as a red-brown band. This band was eluted with acetone. Removal of acetone from the filtered dark red eluate left a mixture of crystals and a dark red liquid. Cooling a filtered solution of this residue in 15 ml. of pentane and 35 ml. of diethyl ether to −78° for 20 hr. precipitated dark red crystals of the product. After filtration and drying, only ~0.06 g. of 1-$C_{14}H_7O_2N_2Mo(CO)_2C_5H_5$ was obtained.

Reaction between p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ and Triphenylphosphine.—A mixture of 0.5 g. (1.49 mmoles) of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$, 0.5 g. (1.91 mmoles) of triphenylphosphine, and 25 ml. of methylcyclohexane was boiled under reflux 1–3 days under nitrogen. Cooling the reaction mixture to room temperature precipitated red crystals of the product.[21] These were filtered and recrystallized twice from a mixture of dichloromethane and hexane at room temperature to give 0.56 g. (66% yield)[22] of red crystalline $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$, m.p. 191–194° dec.

Anal. Calcd. for $C_{31}H_{27}MoN_2OP$: C, 65.3; H, 4.7; N, 4.9; P, 5.4; Mo, 16.8. Found: C, 64.5; H, 4.8; N, 4.8; P, 5.1; Mo, 16.5.

Infrared Spectrum.[23]—Carbon–hydrogen stretching frequency at 3000 (vvw) cm.$^{-1}$; metal carbonyl band at 1860 (s) cm.$^{-1}$; other bands at 1595 (vw), 1511 (m), 1472 (s), 1429 (w), 1275 (vw), 1200 (vvw), 1182 (w), 1138 (w), 1087 (w), 1023 (vw), 1002 (vw), 995 (sh), 815 (w), 798 (w), 790 (sh), 750 (sh), 741 (w), 700 (sh), and 692 (m) cm.$^{-1}$.

Reaction between p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ and Dimethyl Disulfide.—A mixture of 1.0 g. (2.98 mmoles) of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$, 2.0 ml. (2.12 g., 22.5 mmoles) of dimethyl disulfide, and 50 ml. of methylcyclohexane was boiled under reflux 1–3 days under nitrogen. Cooling to room temperature deposited a brown solid which was removed by filtration after several hours. After two crystallizations of this solid from mixtures of dichloromethane and hexane, 0.3–0.5 g. (31–51% yield) of brown crystalline $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$, dec. >175°, was obtained.

Anal. Calcd. for $C_{26}H_{30}Mo_2N_4S_2$: C, 47.7; H, 4.6; N, 8.6; S, 9.8; O, 0.0; Mo, 29.4; mol. wt., 654. Found: C, 46.4, 44.4; H, 4.5, 4.3; N, 8.4, 8.6; S, 9.8, 9.2; O, 1.4, 2.6; Mo, 29.6, 30.4; mol. wt., 675.

Infrared Spectrum.—Carbon–hydrogen stretching frequencies at 3040 (vvw), 2960 (vvw), and 2875 (vw) cm.$^{-1}$; other bands at 1495 (s), 1448 (vs), 1415 (sh), 1370 (w), 1350 (vw), 1293 (w), 1275 (w), 1204 (w), 1188 (m), 1150 (m), 1099 (vw), 1053 (vw), 1011 (vw), 996 (vw), 945 (w), 829 (w), 808 (s), 800 (s), and 742 (w) cm.$^{-1}$.

Ultraviolet and Visible Spectra.—(Maxima in mμ; extinction coefficients in parentheses): (A) $C_6H_5N_2Mo(CO)_2C_5H_5$ (cyclohexane solution): 215 (25,500), 296 (43,300), and 419 (7690); (B) p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ (cyclohexane solution): 217 (26,600), 297 (41,800), and 421 (8740); (C) p-$CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$ (cyclohexane solution): 222 (28,000), 302 (39,200), and 424 (9700); (D) p-$O_2NC_6H_4N_2Mo(CO)_2C_5H_5$ (cyclohexane solution): 245 (21,900), 294 (14,200), 341 (13,300), and 446 (15,700); (E) $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ (dioxane solution): 264 (7620), 272 (7200), and 419 (3720); (F) $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$ (cyclohexane solution): 208 (50,100), 280 (37,400), 330 (27,900), and 430 (10,530).

Discussion

The cyclopentadienylarylazodicarbonylmolybdenum compounds described in this paper are red[24] water-insoluble solids which are slightly air-sensitive. Upon exposure to air for several days they gradually darken. Solutions in organic solvents are somewhat more air-sensitive, depositing a black precipitate over a period of hours. Since pure samples could be obtained by proper use of chromatography and recrystallization, sublimation was avoided as a routine technique of purification.[25] However, in order to check the volatility of this new class of complexes a 0.5894-g. sample of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ was sublimed at 0.1 mm. Slow volatilization occurred at 70° at this pressure. Raising the temperature to 110° caused rapid sublimation to give a dark red sublimate demonstrated by its proton n.m.r. spectrum to be pure unchanged p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$. The recovery of the sublimate was 73%, indicating reasonable thermal stability of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$. The conductivity of a 4.15×10^{-4} M solution of p-$CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$ in acetone was no higher than that of pure acetone excluding any ionic formulations.

The infrared spectra of all of the $RN_2Mo(CO)_2C_5H_5$ compounds exhibit two strong metal carbonyl stretching frequencies in cyclohexane solution similar to other molybdenum carbonyl derivatives of the type $TMo(CO)_2C_5H_5$ In our communication[2] we suggested that ν_{NN} in p-$CH_3OC_6H_4N_2Mo(CO)_2C_5H_5$ occurred at 1600 cm.$^{-1}$. Interpretation of this region of the infrared spectrum, however, was difficult owing to the presence of several absorptions arising from the aromatic nucleus. Examination of the infrared spectra of all of the arylazo compounds of molybdenum described in this paper

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(20) Use of a 2 × 50 cm. alumina column in this preparation results in an incomplete separation.

(21) If a noncrystalline material separates, cooling the mixture at −10° for a few hours will cause it to crystallize.

(22) In an experiment on ten times the indicated scale, a 91% yield of $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ was obtained.

(23) The metal carbonyl region of this infrared spectrum was obtained in a halocarbon oil mull and recorded on a Beckman IR-9 spectrometer. The ermainder of this spectrum was obtained in a KBr pellet and recorded on a Perkin-Elmer Model 21 spectrometer.

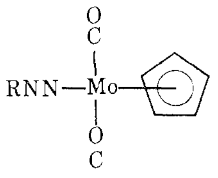
(24) The p-nitrophenylazo derivative is more deeply colored than the other arylazo derivatives of the type $RN_2Mo(CO)_2C_5H_5$. In the crystalline state it is brown with a peculiar greenish tinge. Parshall[11] likewise noted that p-$O_2NC_6H_4N_2PtCl[P(C_2H_5)_3]_2$ was green.

(25) Compounds of the type $RN_2Mo(CO)_2C_5H_5$ like azobenzene appear to be relatively nonexplosive. We have had no explosions during the course of the work described in this paper taking only the usual precautions of synthetic organometallic chemistry.

casts doubt as to the location of ν_{NN}. Although all of the compounds of the type $RN_2Mo(CO)_2C_5H_5$ exhibit medium to strong infrared bands in the range 1615 to 1590 cm.$^{-1}$ (KBr), corresponding bands are not present in $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ or $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$. However, all five $RN_2Mo(CO)_2C_5H_5$ compounds exhibit medium to strong bands in the range 1545 to 1530 cm.$^{-1}$ (KBr). Correspondingly, $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ and $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$ exhibit strong bands at 1472 and 1493 cm.$^{-1}$, respectively. This decrease in frequency upon replacing carbonyl groups with phosphorus or sulfur ligands is in accord with the effect on ν_{CO} and provides evidence for assignment of these other bands to ν_{NN}. In any case the position of ν_{NN} remains doubtful until infrared data on transition metal–alkylazo derivatives with either no aromatic rings[26] or ^{15}N[27] become available.[28]

The proton n.m.r. spectra of the various arylazomolybdenum compounds (Table III) exhibit the expected resonances from both the aryl groups and the π-cyclopentadienyl ligands. Their interpretation is routine. The ability to obtain n.m.r. spectra with normal chemical shifts indicates the diamagnetism of the compounds described in this paper, suggestive of an inert gas configuration for the molybdenum atom.

The proton n.m.r., infrared, and conductivity data cited in the above paragraphs are all in accord with the expected structure I for the $RN_2Mo(CO)_2C_5H_5$ compounds. If the molybdenum atom has the inert gas configuration (as indicated by the diamagnetism) and if the π-cyclopentadienyl and carbonyl ligands donate their usual five and two electrons, respectively, to the molybdenum atom, then the *neutral*[29] RN_2 ligands must be acting as three-electron donors. The $RN_2Mo(CO)_2C_5H_5$ compounds are therefore isoelectronic with the known compounds $C_5H_5Mo(CO)_2NO$,[15,30] $C_5H_5Mo(CO)_2C_3H_5$,[31] $C_5H_5Mo(CO)_2CH_2SCH_3$,[32] and $C_5H_5Mo(CO)_2C_7H_7$.[33] The relationship between the $RN_2Mo(CO)_2C_5H_5$ compounds and $C_5H_5Mo(CO)_2NO$ is especially close since replacement of the oxygen atom in the NO ligand with an arylimino group gives the RN_2 ligand.


I

In carrying out the preparation of the $RN_2Mo(CO)_2C_5H_5$ compounds from $NaMo(CO)_3C_5H_5$ and a solid diazonium salt as described in the Experimental Section, it is necessary that the solid diazonium salt be added slowly to excess $NaMo(CO)_3C_5H_5$.[18] At least in the cases of the phenyl and *p*-anisyl derivatives addition of solid diazonium salt in one portion to an equivalent quantity of a tetrahydrofuran solution of $NaMo(CO)_3C_5H_5$ failed to give any of the corresponding $RN_2Mo(CO)_2C_5H_5$ compound. Instead, most of the diazonium salt and $[C_5H_5Mo(CO)_3]^-$ was converted to a red-purple solid insoluble in pentane and benzene but soluble in tetrahydrofuran. Attempted recrystallization of this material was unsatisfactory. Furthermore, its behavior during recrystallization (*i.e.*, solidifying to a material of amorphous appearance only after complete removal of solvent) suggested an ill-defined polymeric product. The infrared spectrum of the red-violet material obtained from $NaMo(CO)_3C_5H_5$ and *p*-anisyldiazonium tetrafluoroborate exhibited no metal carbonyl bands but strong absorption in ther ange 1420–1385 cm.$^{-1}$ indicative of BF_4^-. Although we do not know what this red-purple solid is, it is clear that it is a tetrafluoroborate salt of a complex, probably polymeric, cation, containing molybdenum but no metal carbonyl groups. Material of similar properties was encountered as a by-product from several attempted reactions of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$, especially with potentially electrophilic reagents such as allyl chloride, heptafluoro-*n*-propyl iodide, and tropylium bromide.

In an attempt to prepare an arylazo derivative of molybdenum containing two molybdenum atoms, the reaction between $[p\text{-}C_6H_4(N_2)_2][BF_4]_2$ and $NaMo(CO)_3C_5H_5$ was investigated. However, the only $RN_2Mo(CO)_2C_5H_5$ compound isolated from this reaction mixture was $C_6H_5N_2Mo(CO)_2C_5H_5$, identified by comparison of its infrared spectrum and melting point with those of authentic $C_6H_5N_2Mo(CO)_2C_5H_5$ obtained from $[C_6H_5N_2][PF_6]$ and $NaMo(CO)_3C_5H_5$. Apparently, one of the diazonium groups in $[p\text{-}C_6H_4(N_2)_2][BF_4]_2$ is replaced by a hydrogen atom in a still unknown manner upon reaction with $NaMo(CO)_3C_5H_5$.

In attempts to prepare arylazo compounds of metals other than molybdenum, reactions between diazonium salts and other metal carbonyl anions including $Mn(CO)_5^-$, $Co(CO)_4^-$, $[C_5H_5W(CO)_3]^-$, $[C_5H_5Fe(CO)_2]^-$, and $V(CO)_6^-$ were investigated. Arylazo compounds similar to those of molybdenum described above were never obtained. The reaction between $NaFe(CO)_2C_5H_5$ and *p*-anisyldiazonium tetrafluoroborate appeared to give largely $[C_5H_5Fe(CO)_2]_2$.

In order to explore the chemistry of $RN_2Mo(CO)_2C_5H_5$, the *p*-tolyl derivative p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ was prepared on a larger scale and its reactions with various materials studied. In general, the car-

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(26) Diazonium salts derived from aliphatic radicals of the usual type (*e.g.*, methyl, ethyl, etc.) are unknown and presumably unstable with respect to loss of nitrogen. Thus the synthetic methods described in this paper are inapplicable for preparation of $RN_2Mo(CO)_2C_5H_5$ compounds with purely aliphatic RN_2^+ ligands. Diazomethane and $HMo(CO)_3C_5H_5$, instead of yielding $CH_3N_2Mo(CO)_2C_5H_5$, give $CH_3Mo(CO)_3C_5H_5$ with loss of nitrogen rather than carbon monoxide.[15]

(27) In this case the effect of substitution of ^{15}N for ordinary ^{14}N on the infrared spectrum could be noted.

(28) Parshall[11] was unable to find any infrared bands attributable to the arylazo ligands in his platinum complexes.

(29) From our experience it is easiest to calculate, understand, and explain the electronic configuration of transition metals in carbonyl and cyclopentadienyl derivatives if all ligands are considered to be *formally* neutral regardless of their charge in the complex. Convenience and clarity are the only reasons that we consider neutral RN_2 ligands in this electron "bookkeeping" process whereas earlier when discussing analogies with nitrosyl and isocyanide complexes we considered positive RN_2^+ ligands.

(30) E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955).

(31) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

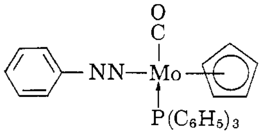
(32) R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964).

(33) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

bonyl ligands in p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ were more easily displaced with other ligands than the carbonyl groups in the related compounds $C_5H_5Mo(CO)_2NO$ and $C_5H_5Mn(CO)_3$. Indeed the carbonyl groups in p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ appear to be as readily displaced by other ligands as those in $C_5H_5Co(CO)_2$.[34,35] For example, reaction between p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ and triphenylphosphine in boiling methylcyclohexane gave a 66% yield of red crystalline $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ (II) entirely analogous to the formation of $C_5H_5CoCOP(C_6H_5)_3$ from $C_5H_5Co(CO)_2$ and triphenylphosphine.[35] Characteristic of $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ is the presence of a single ν_{CO} frequency in the infrared spectrum; its proton n.m.r. spectrum, observable only with difficulty in acetone-d_6 solution, also confirmed the expected structure II.

Cyclopentadienyldicarbonylcobalt reacts with dimethyl disulfide to give black $[CH_3SCoC_5H_5]_2$ (III), presumed to have both two CH_3S bridges and a cobalt–cobalt bond.[34] Similarly, p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ reacts with dimethyl disulfide to give brown $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$, apparently with the related structure IV. The proton n.m.r. spectrum of $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$, besides indicating diamagnetism at least in solution, confirms the presence of p-tolylazo, cyclopentadienyl, and CH_3S ligands in this complex in the ratios 1 : 1 : 1.

Other reactions of p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ do not appear to be as simple as the corresponding reactions of $C_5H_5Co(CO)_2$. Allyl iodide and heptafluoro-n-propyl iodide, both of which react with $C_5H_5Co(CO)_2$ to form well-defined products in good yields,[34,36] give complex red-purple materials similar to those described above. Iodine, which reacts with $C_5H_5Co(CO)_2$ to give $C_5H_5CoCOI_2$,[35,37] reacts with p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ with immediate gas evolution and precipitation of a black solid containing no metal carbonyl groups (infrared spectrum) and possessing the approximate composition $[p\text{-}CH_3C_6H_4N_2MoI_2C_5H_5]_n$. Further studies on this complex are in progress.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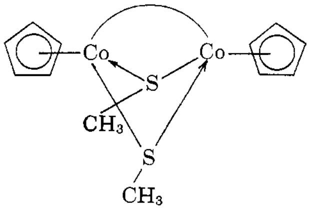
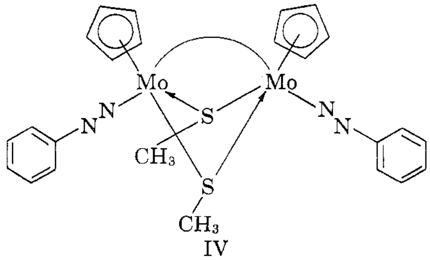

III


IV

A possible explanation for the observed experimental difficulties in the preparation of an extensive series of arylazo derivatives of metal carbonyls corresponding to known metal carbonyl nitrosyls[38] is suggested by the relative ease of displacement of carbonyl groups in p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ by Lewis bases such as triphenylphosphine implying labilization of the metal–carbonyl bond by the presence of an arylazo ligand attached to the same metal atom. This labilization of the metal–carbonyl bond in the $RN_2Mo(CO)_2C_5H_5$ compounds is further supported by the higher ν_{CO} frequencies of the $RN_2Mo(CO)_2C_5H_5$ compounds as compared with other $TMo(CO)_2C_5H_5$ compounds (*e.g.*, in cyclohexane solution ν_{CO} of $CH_3SCH_2Mo(CO)_2C_5H_5$[32] appear at 1952 (s) and 1869 (s) cm.$^{-1}$ compared with the ν_{CO} bands for the $RN_2Mo(CO)_2C_5H_5$ compounds listed in Table II). The higher ν_{CO} frequencies imply a higher carbon–oxygen bond order, implying a lower metal–carbon bond order, indicating less partial $d\pi$–$p\pi$ double bonding and therefore a weaker bond between the metal and carbonyl groups. The arylazo ligand thus appears to increase the positive charge on the metal atom. This inhibits the partial metal–carbonyl double bonding with the resulting weakening of this bond.[39]

Metal carbonyl derivatives of the type $C_5H_5M(CO)YZ$ with one cyclopentadienyl ligand, one carbonyl group, and exactly two other monodentate ligands (which may also be carbonyl groups) appear to have the most stable[40] metal–carbon monoxide bonds found in neutral compounds. For example ultraviolet irradiation is necessary in almost all cases to effect substitution of $C_5H_5Mn(CO)_3$.[41] The arylazo derivatives $RN_2Mo(CO)_2C_5H_5$ are also of this favored type $C_5H_5M(CO)YZ$ ($M = Mo$, $Y = CO$, $Z = RN_2$) but still lose carbon monoxide on treatment with triphenylphosphine or dimethyl disulfide at 100°. Owing to the labilization of metal–carbon monoxide bonds by arylazo groups discussed above, arylazometal carbonyls of less favored types such as $RN_2V(CO)_5$, $RN_2Mn(CO)_4$, $RN_2FeCOC_5H_5$, $RN_2Co(CO)_3$ are likely to have metal–carbon monoxide bonds so weak that under conditions required for the formation[42] of these arylazo–metal car-

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[34] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[35] R. B. King, paper presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, Abstracts, p. 21-O; R. B. King, *Inorg. Chem.*, **5**, 82 (1966).

[36] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16b**, 475 (1961); R. F. Heck, *J. Org. Chem.*, **28**, 604 (1963).

[37] R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964); R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

[38] The range of existence of metal carbonyl nitrosyls is more limited than that of the isoelectronic compounds containing a carbonyl ligand in place of the nitrosyl ligand. Thus the compounds $V(CO)_5NO$ and $C_5H_5FeCONO$, isoelectronic with the stable species $Cr(CO)_6$ and $C_5H_5Co(CO)_2$, respectively, have not yet been isolated. Data presently available suggest that in isoelectronic series the stability decreases in the order CO (most stable) > NO > RN_2 (least stable).

[39] This effect is similar to that of the charge on the metal atom weakening the metal–carbon monoxide bond in metal carbonyl cations (*e.g.*, $Mn(CO)_6^+$) and strengthening the metal–carbon monoxide bond in metal carbonyl anions (*e.g.*, $V(CO)_6^-$).

[40] Here stability of the carbonyl groups with respect to replacement with other ligands is meant.

[41] E. O. Fischer and M. Herberhold in "Essays in Coordination Chemistry" (Experientia Supplement IX), Birkhäuser Verlag, Basel, 1964, p. 259.

[42] Potential reagents for the decomposition of the arylazo–transition metal compounds obtained from diazonium salts and metal carbonyl anions are excess of the diazonium salt and the basic ether solvent (*e.g.*, tetrahydrofuran). Indeed, action of excess diazonium salt appears to destroy even the $RN_2Mo(CO)_2C_5H_5$ compounds.[18]

bonyls, the metal–carbon monoxide bonds are broken resulting in decomposition of the arylazo–metal carbonyls. We feel that this effect presents a severe impediment to the preparation of extensive series of arylazo–metal carbonyls.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-64. We are also indebted to Mr. A. Fronzaglia for assistance with the infrared spectra.

Notes

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

Organonitrogen Derivatives of Metal Carbonyls. III. Reactions between Metal Carbonyl Anions and Chloromethyl Isocyanate[1]

BY R. B. KING AND M. B. BISNETTE

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Recently we reported reactions of metal carbonyl anions with haloalkyl sulfides[2] and haloalkyl amines.[3] We have now extended our studies of haloalkyl derivatives containing potentially reactive functional groups to chloromethyl isocyanate. This note describes the reactions of chloromethyl isocyanate with the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$.

Experimental Section

The general techniques used for infrared spectra, proton n.m.r. spectra, elemental microanalyses, and molecular weight determinations were similar to those used for work described in previous papers.[1,2] As before tetrahydrofuran was freshly distilled over lithium aluminum hydride. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with organometallic compounds, (b) admitting to evacuated flasks and other vessels, and (c) handling filtered solutions of organometallic compounds. Chromatographic separations were carried out on 80–200 mesh adsorption alumina (Fisher Scientific Co., No. A 540).

The chloromethyl isocyanate, b.p. 81° (740 mm.), was prepared in 49% yield[4] by reaction between chloroacetyl chloride and sodium azide in triethylene glycol dimethyl ether[5] at ~25°. The preparations of the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$ have been adequately described.[6,7]

Reaction between $NaMo(CO)_3C_5H_5$ and Chloromethyl Isocyanate.—A solution of 10 mmoles of $NaMo(CO)_3C_5H_5$ in 100 ml. of tetrahydrofuran was prepared from $[C_5H_5Mo(CO)_3]_2$ and dilute sodium amalgam. This solution was stirred ~16 hr. with 1.0 g. (10.9 mmoles) of chloromethyl isocyanate. Solvent was removed from the brownish reaction mixture at 25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at ~25° (30 mm.). The brown residue was extracted with 100 ml. of pentane in six portions and the filtered pentane extracts were cooled 16 hr. at −78°. Yellow crystals of $C_5H_5Mo(CO)_3CH_2NCO$ separated. These crystals were removed by filtration and recrystallized similarly from pentane to give 0.542 g. (18% yield) of yellow crystalline $C_5H_5Mo(CO)_3CH_2NCO$, m.p. 53–56°.

For the preparation of larger quantities of $C_5H_5Mo(CO)_3CH_2NCO$ a solution of 100 mmoles of $NaMo(CO)_3C_5H_5$ in 500 ml. of tetrahydrofuran prepared from hexacarbonylmolybdenum and a 20% excess of sodium cyclopentadienide was similarly allowed to react with 11.0 g. (121 mmoles) of chloromethyl isocyanate. The product was isolated by a procedure similar to that used for the smaller scale preparation cited above except that a mixture of pentane and diethyl ether rather then pure pentane was used for crystallizations in order to diminish the required amount of solvent. This larger scale preparation gave a total of 12.6 g. (42% yield) of $C_5H_5Mo(CO)_3CH_2NCO$ isolated in two crops.

When freshly recrystallized, $C_5H_5Mo(CO)_3CH_2NCO$ forms yellow crystals, which soon darken on standing. It can be sublimed at 100° (0.2 mm.). A 15% recovery of yellow-orange sublimate, m.p. 54–56°, is obtained, shown by its infrared and n.m.r. spectra to be unchanged $C_5H_5Mo(CO)_3CH_2NCO$.[8]

Anal. Calcd. for $C_{10}H_7MoNO_4$: C, 39.9; H, 2.3; N, 4.7; Mo, 31.9; O, 21.3. Found: C, 39.9; H, 2.2; N, 4.5; Mo, 32.7; O, 20.8.

Infrared Spectrum.[9]—ν_{CH} at 3050 (vw), 2870 (vvw), and 2820 (vvw) cm.$^{-1}$; ν_{CN} (isocyanate) at 2270 (s) cm.$^{-1}$; ν_{CO} (metal) at 2033 (m), 1959 (s), and 1950 (s) cm.$^{-1}$; other bands at 1460 (w), 1415 (w), 1225 (vw), 1142 (w), 1054 (w), 1005 (w), 1001 (w), 848 (w), 836 (m), 819 (m), and 812 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum (CS_2 Solution).—Singlet resonances at τ 4.57 and 6.31 of approximate relative intensities 5:2 due to the five π-cyclopentadienyl protons and the two methylene protons, respectively.

Reaction between $NaFe(CO)_2C_5H_5$ and Chloromethyl Isocyanate.—A solution of 50 mmoles of $NaFe(CO)_2C_5H_5$ in 150 ml. of tetrahydrofuran was treated dropwise with 4.5 g. (50 mmoles) of chloromethyl isocyanate. An exothermic reaction occurred with gas evolution. After stirring for ~16 hr. at room temperature solvent was removed at ~25° (30 mm.). The residue was extracted with five 75-ml. portions of dichloromethane, and solvent was removed from the filtered dichloromethane extracts leaving a brown residue. This residue was extracted with ~100 ml. of diethyl ether in four portions and the filtered diethyl ether solution chromatographed on a 2 × 50 cm. alumina column. Four bands were observed in the indicated order: yellow-orange (I), purple-brown (II), brown (III), and green-black (IV). The green-black band (IV) was so weak that it was not further investigated. The other three bands were eluted with diethyl

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(1) For Part II of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

(2) R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965).

(3) R. B. King and M. B. Bisnette, Abstracts of Papers presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 43M; *Inorg. Chem*., **5**, 293 (1966).

(4) G. Schroeter, *Ber.*, **42**, 3356 (1909).

(5) Triethylene glycol dimethyl ether, b.p. 216°, was used instead of the di-*n*-amyl ether, b.p. 188°, specified by Schroeter.[4]

(6) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, and references cited therein.

(7) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(8) Other molybdenum complexes such as $C_3F_7COMo(CO)_3C_5H_5$ and $CH_3SCH_2Mo(CO)_3C_5H_5$ are decarbonylated under these conditions.[2,7]

(9) The metal carbonyl region of this infrared spectrum was taken in a cyclohexane solution and recorded on a Beckman IR-9 spectrometer with the scale expanded by a factor of 2.5. The remaining portion of this infrared spectrum was taken in a potassium bromide pellet and recorded on a Perkin-Elmer Model 21 spectrometer.