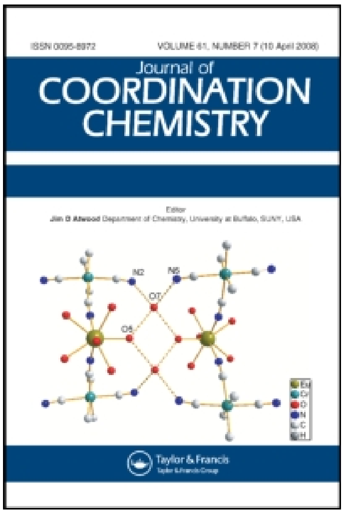

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COMPLEXES OF 1,8-NAPHTHYRIDINES IX. GROUP VIb METAL CARBONYL COMPLEXES CONTAINING 1,8-NAPHTHYRIDINE, 2-METHYL-1,8-NAPHTHYRIDINE OR *trans*-DECAHYDRO-1,8-NAPHTHYRIDINE

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COMPLEXES OF 1,8-NAPHTHYRIDINES IX. GROUP VIb METAL CARBONYL COMPLEXES CONTAINING 1,8-NAPHTHYRIDINE, 2-METHYL-1,8-NAPHTHYRIDINE OR *trans*-DECAHYDRO-1,8-NAPHTHYRIDINE[1a]

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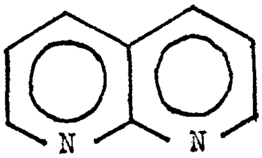
Complexes of the type $M(CO)_5(N{-}N)$, $M(CO)_4(N{-}N)$ and $M(CO)_3(N{-}N)_2$, where M is Cr, Mo or W and N–N is 1,8-naphthyridine(napy), 2-methyl-1,8-naphthyridine(2-mnapy) or *trans*-decahydro-1,8-naphthyridine(dhnapy), have been prepared and characterized by infrared and proton magnetic spectroscopy. Complexes of the type $Mo(CO)_3(N{-}N)(napy)$, where N–N is 1,10-phenanthroline(phen), 2,2′-bipyridine(bipy), 2,9-dimethyl-1,10-phenanthroline(2,9-dmphen) or 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy), were also prepared and characterized by infrared spectroscopy. In these systems, the various naphthyridine donors exhibit the unique ability to behave as both mono- and bidentate ligands. The mode of bonding between the metal and heterocycles is determined by proton magnetic resonance data.

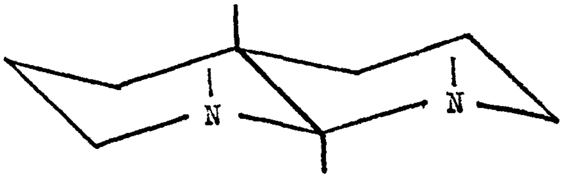
INTRODUCTION

Thermal reactions between the Group IVb hexacarbonyls and 2,7-dimethyl-1,8-napthyridine(2,7-dmnapy) produce tetracarbonyl complexes[2] while further reactions of these tetracarbonyl complexes with various monodentate Lewis bases produce mixed-ligand tri- and dicarbonyl complexes.[3] Coordination of 2,7-dmnapy to a metal in a bidentate manner results in the formation of a four-membered-ring chelate system in the complex. Several other systems containing a bidentate 1,8-naphthyridine heterocycle (1) which have been investigated involve metals in the +1, +2 and +4 oxidation states.[4,5,6] However, no comparison of coordination behavior of napy and 2,7-dmnapy with metals in the zero oxidation state has been reported.



(1)
napy

The isolation of carbonyl complexes wherein a potential bidentate nitrogen donor ligand behaves in a monodentate manner is extremely rare for flexible molecules such as ethylenediamine or 2,2′-bipyridine(bipy)[7] and for rigid systems such as 1,10-phenanthroline, only a single example is to be found.[8]



(2)
dhnapy

In this paper, we report the preparation and characterization of complexes containing 1,8-naphthyridine, 2-methyl-1,8-naphthyridine (2-mnapy), and *trans*-decahydro-1,8-naphthyridine(2) wherein the naphthyridine systems exhibit both mono- and bidentate behaviour.

RESULTS AND DISCUSSION

The majority of the pentacarbonyl derivatives of the Group VIb hexacarbonyls are synthesized *via* an ultraviolet irradiation of a mixture of the hexacarbonyl and ligand.[9] When this method is employed with the naphthyridine systems, the results are the exclusive formation of $Mo(CO)_3(N\text{–}N)_2$. A donor exchange method,[8] however, does afford the pentacarbonyl complexes. The yields are fairly low (approximately fifty percent for the tungsten derivatives) and decrease in the order $W > Cr \gg Mo$. If a direct thermal reaction between $M(CO)_6$ and napy is interrupted shortly after initiation, evidence for a mixture of mono-, di- and trisubstituted derivatives of chromium and tungsten, or a trisubstituted complex of molybdenum is obtained through the use of infrared spectroscopy. Isolation of the pentacarbonyl complexes from these mixtures cannot be achieved due to the decomposition of the complexes in solution.

The positions and intensities of the carbonyl absorptions are characteristic of pentacarbonyl complexes in an octahedral environment,[10] which implies that the heterocyclic ligands are functioning in a monodentate manner. The carbonyl stretching frequencies of the naphthyridine containing pentacarbonyl complexes (Table I) are

TABLE I

Carbonyl stretching frequencies[a]

Compound	νCO (cm^{-1})			
	A_1	B_1	E	A_1
$Cr(CO)_5$(napy)	2068 m	1985 sh, w	1935 s	1887 sh, s
$Cr(CO)_5$(2-mnapy)	2066 m	1984 sh, m	1932 s	1886 sh, s
$Cr(CO)_5$(dhnapy)[b]	2065 m	1978 sh, w	1928 s	1892 sh, s
$Mo(CO)_5$(napy)[b]	2074 m	1985 sh, w	1938 s	1886 sh, s
$Mo(CO)_5$(2-mnapy)[b]	2072 m	1984 sh, m	1936 s	——
$Mo(CO)_5$(dhnapy)[b]	2075 m	1984 sh, w	1937 s	1905 sh, s
$W(CO)_5$(napy)	2073 m	1979 sh, w	1928 s	1885 sh, s
$W(CO)_5$(2-mnapy)	2071 m	1978 sh, m	1924 s	1884 sh, s
$W(CO)_5$(dhnapy)	2074 m	1976 sh, w	1927 s	1893 sh, s
	A_1	B_1	A_1	B_2
$Cr(CO)_4$(napy)[b]	2016 m	1899 s	1885 sh, s	1838 m
$Cr(CO)_4$(2-mnapy)	2015 m	1905 s	1885 sh, s	1836 m
$Cr(CO)_4$(2,7-dmnapy)	2016 m	1905 s	1884 sh ,s	1836 m
$Cr(CO)_4$(dhnapy)[b]	2009 m	1889 s	1859 sh, s	1812 m
$Mo(CO)_4$(napy)[b]	2024 m	——	1885 sh, s	1837 m
$Mo(CO)_4$(2-mnapy)	2022 m	1914 s	1882 sh, s	1835 m
$Mo(CO)_4$(2,7-dmnapy)	2021 m	1910 s	1882 sh, s	1836 m
$Mo(CO)_4$(dhnapy)[b]	2009 m	1890 s	1862 sh, s	1815 m
$W(CO)_4$(2-mnapy)	2015 m	1899 s	1875 sh, s	1832 m
$W(CO)_4$(2,7-dmnapy)	2012 m	1897 s	1975 sh, s	1831 m
$W(CO)_4$(dhnapy)[b]	1999 m	1976 s	1850 sh, s	1808 m
	A_1'	A_2'	A''	
$Cr(CO)_3(napy)_2$	1895 s	1775 s	1752 s	
$Mo(CO)_3(napy)_2$	1900 s	1781 s	1754 s	
$W(CO)_3(napy)_2$	1890 s	1777 s	1745 s	
$Mo(CO)_3(2\text{-mnapy})_2$	1897 s	1778 s	1754 s	
$W(CO)_3(2\text{-mnapy})_2$	1887 s	1869 s	1745 s	
$Mo(CO)_3$(2,7-dmnapy)(napy)[b]	1990 s	1778 s	1748 s	
$Mo(CO)_3$(phen)(napy)	1893 s, br	1778 s	1746 s	
$Mo(CO)_3$(dipy)(napy)	1889 s, br	1780 s	1756 s	
$Mo(CO)_3$(2,9-dmphen)(napy)	1890 s, br	1779 s	1759 s	

[a] Recorded in chloroform for $M(CO)_5L$ and $M(CO)_4L$ compounds and in Nujol for $M(CO)_3L_2$ compounds.

[b] Although identified by their infrared spectra, not isolated as pure substances.

nearly identical to those of analogous complexes, which contain non-heterocyclic nitrogen donor-ligands, such as cyclohexylamine, ethylenediamine and dhnapy.[11, 12]

Attempts to prepare $M(CO)_4(napy)$ by direct thermal or photochemical reactions were unsuccessful. Evidence indicating the existence of these tetracarbonyl complexes is obtained from the solution infrared spectra of the corresponding $M(CO)_3(napy)_2$ complexes after disproportionation has commenced. The tetracarbonyl intermediates cannot be isolated as they decompose quite rapidly affording $M(CO)_5(napy)$, which in turn disproportionates to yield $M(CO)_6$ and napy. The 2-mnapy system exhibits properties characteristic of both napy and 2,7-dmnapy in that complexes with the formulation $M(CO)_5(2\text{-mnapy})$, $M(CO)_4(2\text{-mnapy})$ and $M(CO)_3(2\text{-mnapy})_2$ can be isolated. Although these complexes are more stable in solution than their napy analogs, they also undergo decomposition.

The carbonyl stretching frequencies for the tetracarbonyl complexes (Table I) indicate, unlike the pentacarbonyl derivatives, considerable difference between the behaviour of the various naphthyridine heterocycles and dhnapy. Indeed, dhnapy appears to be similar to ethylenediamine while the naphthyridines are more like pyridine.

The carbonyl stretching frequencies of the tricarbonyl complexes are presented in Table I. We were unable to prepare any tricarbonyl derivatives containing dhnapy or the chromium derivative of 2-mnapy. It is probable that the high basicity of dhnapy, its inability to backbond and steric requirements prevent coordination of two dhnapy moieties to the metal. It is also likely that steric crowding of the methyl groups hinders coordination of two 2-mnapy ligands to the smaller chromium.

Reactions between $M(CO)_4(N\text{–}N)$, where N–N is phen, bipy, 2,9-dmphen or 2,7-dmnapy and napy produce complexes of the type $Mo(CO)_3(N\text{–}N)$ (napy). The νCO data indicate that these octahedral complexes are of *fac* configuration which implies that napy is again acting in a monodentate fashion. Although there is no evidence for the replacement of any of the five-membered-ring chelates by napy, all attempts to prepare $Mo(CO)_3(2,7\text{-dmnapy})(napy)$ resulted in the replacement of some of the 2,7-dmnapy by napy. The stability of the five-membered systems may result from conjugation with the metal which cannot occur with the naphthyridines and less ring strain. The $M(CO)_3L_2(L = napy$ or 2-mnapy) series presents a unique case wherein the ligand behaves both in a mono and bidentate fashion in the same complex.

TABLE II

Pmr data for 1,8-naphthyridine and 2-methyl-1,8-naphthyridine complexes

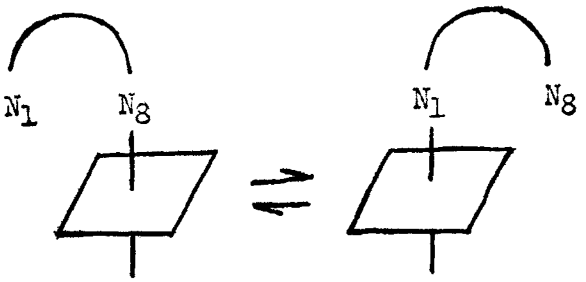
Compound	Chemical Shifts (δ)[a]					
		2,7-H	4,5-H		3,6-H	
napy		9.09	8.20		7.47	
$Cr(CO)_5(napy)$		9.38	8.28		7.52	
$W(CO)_5(nappy)$		9.46	8.35		7.55	
	7-H	6-H	5-H	4-H	3-H	2-CH
2-mnapy	8.96	7.32	8.05	7.97	7.27	2.73
$Cr(CO)_5(2\text{-mnapy})$	9.42	7.32	8.24	8.12	7.41	2.88
$W(CO)_5(2\text{-mnapy})$	9.60	7.37	8.34	8.13	7.48	2.87
$Cr(CO)_4(2\text{-mnapy})_2$	8.75	7.47	8.12	8.04	7.41	2.73
$Mo(CO)_4(2\text{-mnapy})_2$	8.84	7.55	8.23	8.17	7.50	2.75
$W(CO)_4(2\text{-mnapy})_2$	8.97	7.55	8.31	8.23	7.51	2.71

[a] Recorded in methylene chloride at normal probe temperature with tetramethyl silane as an internal reference.

Table II presents the pmr data for the free and complexed napy and 2-mnapy heterocycles. The protons of the heterocyclic ligands in the pentacarbonyl derivatives are deshielded with respect to the free ligand, with the 2- and 7-protons in the napy complexes and the 7-proton in the 2-mnapy complexes being the most drastically deshielded. In contrast, the methyl protons of the tetracarbonyl complexes retain about the same electron density as in the free ligand while the 7-proton becomes shielded. The magnitude of the differences in the electron density about the protons closest to the metal suggests that the bonding modes in the penta- and tetracarbonyl complexes are quite different indeed.

From a comparison of the pmr data of $Mn(CO)_3(2\text{-mnapy})Cl$ and $Re(CO)_3(2\text{-mnapy})Cl$[4] with the $M(CO)_4(2\text{-mnapy})$ derivatives reported herein, it is evident that bidentate coordination of the heterocycle results in shielding of the proton at the seven-position. The shielding of the proton at the seven-position is partly due to the loss of the anisotropic deshielding effect of the lone pair of electrons on the *alpha*-nitrogen, but may also be due to the anisotropy of the near by carbonyl group and/or to metal-non-bonded hydrogen interactions. Since the 7-proton of 2-mnapy in $M(CO)_5(2\text{-mnapy})$ is drastically deshielded, this suggests that the anisotropic deshielding effect of the lone pair of electrons on nitrogen is still present and/or that this proton is now in the vicinity of a deshielding region of the adjacent carbonyl groups. In addition to this information, the magnitude of deshielding of the methyl protons in $M(CO)_5$(2-mnapy) relative to the free ligand is almost exactly the same as the magnitude of deshielding of the methyl protons in $Mn(CO)_3$(2-mnapy)Cl.[4] These data indicate that only one nitrogen is coordinated to the metal, and furthermore, that the nitrogen closest to the methyl group is coordinated to the metal in the pentacarbonyl complexes. Coordination of the 1-nitrogen is expected since it is the more basic of the two potential donor atoms.[13]

The pmr spectra of $Mn(CO)_3$(napy)X, X = Cl, Br, wherein napy is bidentate exhibits shielding of the 2- and 7-protons[4] while the 7-proton in $M(CO)_5$(2-mnapy) where coordination is monodentate (N_1), is deshielded. The broad, poorly resolved 2- and 7-proton signals of $M(CO)_5$napy lie at an intermediate value. The resonance shapes suggest rapid exchange between the two possible metal-nitrogen bonding modes. Unfortunately, decreased solubility at lower temperature prevented freezing out the exchange.



CONCLUSION

The complexes reported herein augment the report by Behrens[8] that rigid, potentially bidentate ligands may behave in a monodentate manner. The first example of a rigid chelate functioning as a mono- and bidentate ligand within the same complex is provided. Thus, the assumption applied in some studies of the mechanisms of metal carbonyl substitution reactions, that the geometry of rigid bidentates demands both donor atoms to be coordinated, seems in question.[14] The effects of steric requirements and basicity cause napy and 2-mnapy to differ more in their coordination properties from 2,7-dmnapy than the latter differs from phen, bipy or 2,9-dmphen.

EXPERIMENTAL SECTION

Materials

Chromium hexacarbonyl was purchased from the Pressure Chemical Company. Molybdenum and tungsten hexacarbonyl were generous gifts of the Climax Molybdenum Company. The procedures of Paudler and Kress were used for the preparation of 1,8-naphthyridine,[15] 2-methyl-1,8-naphthyridine,[15] 2,7-dimethyl-1,8-naphthyridine[13] and *trans*-decahydro-1,8-naphthyridine.[16] All other nitrogen heterocycles are commercially available (Eastman Chemical) and were used without further purification. All solvents were ACS grade which had been dried and stored over molecular sieves and/or sodium.

Preparations

$Mo(CO)_4$(2,7-dmnapy) and $Mo(CO)_4$(2,9-dmphen) were prepared as outlined elsewhere.[2]

$Mo(CO)_4$(phen) and $Mo(CO)_4$(bipy) were prepared by the method of Stiddard.[17] Complexes of the type $M(CO)_5$(N-N), where M is Cr, Mo or W and N-N is napy, 2-mnapy or dhnapy, were all prepared in a manner similar to that for the chromium derivative: Chromium hexacarbonyl (0.44 g, 2.0 mmol) in 30 ml of absolute methanol was irradiated with uv light (Hanovia Model 765-1) for 5 hr under a nitrogen atmosphere. To this solution was added 1,8-naphthyridine (0.26 g, 2.00 mmol), and the solvent was removed by vacuum evaporation. The crude product, in a 10 ml cyclohexane slurry, was loaded onto an alumina-filled column (Fisher A-540, 200–800 mesh alumina was loaded into the chromatography column from a cyclohexane slurry until a column 25 cm in length was obtained) and eluted with 20 ml of methylene chloride. The methylene chloride fraction was concentrated by vacuum evaporation until a precipitate formed, which was collected on a filter. The organge-red complex was washed with three 5-ml portions of 0.1 N hydrochloric acid and dried *in vacuo*. Complexes of the type $M(CO)_4$(2-mnapy), where M is Cr, Mo or W were prepared by refluxing the parent hexacarbonyl and ligand (1:2) in 30 ml of xylene under a helium atmosphere for 2 hr. After the solution cooled to room temperature, it was filtered and the filtrate was treated with 20 ml of hexane and cooled to −78°. The precipitate that formed was collected on a filter and dried *in vacuo.* Complexes of the type $M(CO)_3(napy)_2$ and $M(CO)_3(2\text{-mnapy})_2$, where M is Cr, Mo or W were prepared by refluxing the parent hexacarbonyl and ligand (1:2) in 30 ml of xylene under a helium atmosphere for 2 hr. The hot solution was filtered under a flush of helium, and the precipitate was washed with 20 ml of pentane and dried *in vacuo.* Complexes of the type $Mo(CO)_3(N\text{–}N)(napy)$, where N–N is phen, bipy, 2,9-dmphen or 2,7-dmnapy, were prepared by refluxing $Mo(CO)_4(N\text{–}N)$ and napy (1:1) in 20 ml of *n*-octane for 4 hr under a helium atmosphere. Isolation was achieved in a manner similar to that for the $M(CO)_3(napy)_2$ complexes. Carbon, hydrogen and nitrogen compositions were ascertained by combustion and the results are given in Table III.

Spectral Measurements

The infrared spectra of the compounds obtained in Nujol Mulls, KBr and CsI pellets (4000–200 cm^{-1}) and saturated chloroform solutions (2200–1600 cm^{-1}) were recorded with a Perkin-Elmer Model 621 double beam grating spectrophotometer. The proton magnetic resonance spectra obtained in saturated methylene chloride solutions with tetramethylsilane as an internal standard were recorded using a Varian HA-100 Spectrometer.

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   b NASA Graduate Trainee.
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TABLE III

Analytical data

Compound	Analyses					
	% Carbon		% Hydrogen		% Nitrogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Cr(CO)_5(napy)$	48.46	48.70	1.87	1.72	8.69	8.83
$W(CO)_5(napy)$	34.39	34.57	1.33	1.29	6.17	6.17
$Cr(CO)_5(2\text{-mnapy})$	50.01	49.73	2.40	2.32	8.33	8.53
$W(CO)_5(2\text{-mnapy})$	35.92	35.78	1.72	1.56	5.98	5.94
$W(CO)_5(dhnapy)$	33.64	33.57	3.46	3.47	6.01	5.80
$Cr(CO)_4(2\text{-mnapy})$	50.66	50.69	2.62	2.42	9.09	9.28
$Mo(CO)_4(2\text{-mnapy})$	44.34	44.35	2.29	2.07	7.95	7.66
$W(CO)_4(2\text{-mnapy})$	35.48	35.33	1.83	1.86	6.37	6.27
$Cr(CO)_3(napy)_2$	57.58	57.50	3.05	3.05	14.14	14.14
$Mo(CO)_3(napy)_2$	51.83	51.77	2.75	2.66	12.73	12.97
$W(CO)_3(napy)_2$	43.20	43.07	2.29	2.19	10.61	10.78
$Mo(CO)_3(2\text{-mnapy})_2$	53.86	54.06	3.44	3.24	11.96	11.92
$W(CO)_3(2\text{-mnapy})_2$	45.35	45.48	2.90	2.92	10.97	10.21
$Mo(CO)_3(phen)(napy)$	56.34	56.31	2.98	2.98	11.43	11.66
$Mo(CO)_3(bipy)(napy)$	54.09	54.47	3.03	3.05	12.01	12.04
$Mo(CO)_3(2,9\text{-dmphen})(napy)$	57.93	57.47	3.59	3.44	10.81	11.10

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