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Tetracarbonylmolybdenum complexes of 2-(phenylhydrazino)pyridine ligands. Correlations of spectroscopic data with pyridyl substituent effects

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Abstract

The 2-(phenylhydrazino)pyridine (2-PHP) complexes *cis*-$Mo(CO)_4$(X–2-(phenylhydrazino)pyridine) (X = 4-CH_3O, 4-CH_3, H, 4-Cl, 5-Br, 6-CH_3, 4,6-$(CH_3)_2$) and *cis*-$Mo(CO)_4$(2-(2-CH_3–phenylhydrazino)pyridine) have been synthesized and characterized. The properties of these complexes are compared with those of the analogous 2-(phenylazo)pyridine (2-PAP) complexes. The lack of the π-accepting azo group in the 2-PHP ligands leads to less stable complexes, including the inability even to isolate the complex with X = CF_3. The 2-PHP complexes show very good correlations among the ^{95}Mo-NMR chemical shift, the sum of the carbonyl stretching frequencies, and the Hammett σ parameter for the pyridyl substituents. There is also an excellent correlation ($r = 0.978$, $n = 7$) of the ^{95}Mo chemical shift of the 2-PHP complexes with the shift for the 2-PAP complexes. The failure of the complexes with X = 6-CH_3 or 4,6-$(CH_3)_2$ or the complex *cis*-$Mo(CO)_4$(2-(2-CH_3–phenylhydrazino)pyridine) to fit some of the correlations is attributed to steric or electronic effects. The 2-hydrazinopyridine complex *cis*-$Mo(CO)_4(H_2NHNC_5H_4N)$ also was characterized.

Keywords: 2-(Phenylhydrazino)pyridine complexes; Molybdenum complexes; Nuclear magnetic resonance

1. Introduction

Among *N*,*N*-chelating ligands, the azoimines which contain –N=N–C=N– linkage are unusual in their ability to stabilize metal centers in their lower oxidation states [1]. This property was first recognized in 2-(phenylazo)pyridine (2-PAP) (**Ic**) and arises from the presence of the azo functionality, which reduces the σ-donating ability of the nitrogen atoms and enhances the π-accepting ability through the azo π* orbital [2–4]. Substituents on the pyridyl ring of 2-PAP can alter these donor and acceptor properties in a systematic manner. Thus, in a study of a series of complexes *cis*-$Mo(CO)_4$(L–L′) (**II**) (L–L′ = substituted 2-PAP (**Ia**–**Ih**)), good correlations were observed between the Hammett sigma parameters of the substituents and the first oxidation potential, the carbonyl-stretching frequencies, and the ^{95}Mo-NMR chemical shift of the complexes [5]. This study concluded that "2-(phenylazo)pyridines might be appropriately viewed as ligands whose strong π-acceptor ability resides with the azo group, while the pyridyl group acts largely as a pyridine whose basicity has been decreased by the strong electron-withdrawing 2-phenylazo substituent". Given the significant role of the azo group on the stability and properties of the complexes, we were interested in the effects if it were removed.

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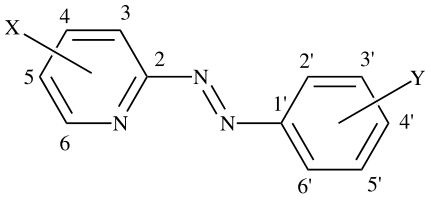

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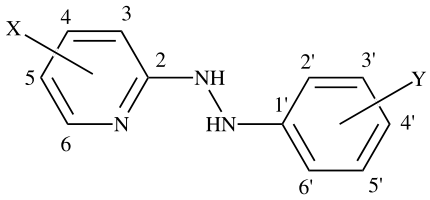


III

a X = 4-CH_3O; Y = H

b X = 4-CH_3; Y = H

c X = Y = H

d X = 4-Cl; Y = H

e X = 5-Br; Y = H

f X = 5-CF_3; Y = H

g = 6-CH_3; Y = H

h X = H; Y = 2'-CH_3

i = X = 4,6-$(CH_3)_2$; Y = H

Accordingly, we have synthesized a series of 2-(phenylhydrazino)pyridine (2-PHP) ligands (**III**) in which the azo group has been reduced to a hydrazino group and have used them to obtain the molybdenum tetracarbonyl complexes. We have also examined the properties of the complexes for correlations among the data collected.

2. Experimental

2.1. General procedures

All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard procedures [6]. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. Infrared spectra were recorded on a Perkin–Elmer Model 1760 spectrophotometer at 1 cm^{-1} resolution. ^{1}H-, ^{13}C-, and ^{95}Mo-NMR spectra were recorded on a Bruker AC200 spectrometer as previously described [5]. Electronic spectra were recorded on a Cary 5E spectrophotometer. Melting points were taken in open capillaries and are uncorrected. Cyclic voltammetry was performed in a three-compartment cell using 0.1 M tetrabutylammonium fluoroborate as the supporting electrolyte in CH_2Cl_2 with ferrocene as an internal standard as previously described [5]. Data reported were recorded at 100 mV s^{-1}.

2.1.1. Synthesis of 2-(phenylhydrazino)pyridines (*III*)

The 2-PHP ligands (**III**) were obtained by reduction of the corresponding 2-PAP [5,7,8] with formamidinesulfinic acid in a basic methanol solution using modifications of the procedure reported for reducing **Ic** and **Ig** [9]. The method used and yield obtained are summarized in Table 1.

2.1.1.1. Method A. Three to six millimoles of 2-PAP (**I**) was dissolved in a mixture of 4 ml of CH_3OH and 1 ml of 15 M NH_3. The solution was kept at 50–55 °C and a 10–20% molar excess of formamidinesulfinic acid was added in portions over 30 min. The red solution gradually lightened in color. Acidity of the solution was monitored with pH paper, and NH_3 was added as needed to keep the solution basic. If a precipitate formed, a minimum amount of CH_3OH was added to dissolve it. When the reaction was complete, the solution was cooled and the precipitated product **III** was collected by filtration and washed with a cold mixture of CH_3OH/H_2O. A second crop of crystals was often obtained by reducing the volume of the filtrate or by adding water to it.

2.1.1.2. Method B. The procedure was similar to that of method A with two exceptions. First, the amounts of CH_3OH and 15 M NH_3 were doubled. Second, at the end of the reaction, the solution was taken to dryness under reduced pressure and the residue was extracted with benzene. The extract was washed with water and dried over Na_2SO_4. Benzene was removed under reduced pressure, and the residue was recrystallized from an acetone–hexane mixture.

2.1.2. cis-Mo(CO)$_4$(4,6-dimethyl-2-(phenylazo)pyridine) (*IIi*)

Compound **IIi** was obtained from the reaction of 1.18 mmol of 4,6-dimethyl-2-(phenylazo)pyridine) (**Ii**) and 1.45 mmol of *cis*-$(C_7H_8)Mo(CO)_4$ (C_7H_8 = norbornadiene) [10] in the manner previously used to obtain similar complexes [5]. The yield was 70% of deep-blue crystals melting at 115–117 °C. IR (hexane) ν(C≡O) 2024m, 1941s, 1931m, 1888m cm^{-1}; Vis (λ_{max}, nm): (hexanes) 617.4; (CH_2Cl_2) 597.6. ^{1}H-NMR ($CDCl_3$, δ): 8.04 (s, 1H, H3), 7.8–7.9 (m, 2H, H2′ and H6′), 7.4–7.6 (m, 3H, H3′, H4′, and H5′), 7.37 (s, 1H, H5), 2.91

Table 1
Yields, melting points, and elemental analyses for 2-(phenylhydrazino)pyridines

Compound	Synthesis method	Yield (%)	Melting point (°C)	Elemental analysis (Found (Calc.), %)		
				C	H	N
IIIa	B	55	118–119	66.96 (67.00)	6.09 (6.02)	19.52 (19.61)
IIIb	A	49	135–137	72.34 (72.18)	6.58 (6.63)	21.09 (21.01)
IIId	B	61	113–114	60.15 (60.24)	4.59 (4.61)	19.13 (19.21)
IIIe	A	53	91–92	50.02 (49.39)	3.82 (3.92)	15.91 (16.13)
IIIf [a]	A	47	115–117			
IIIh	B	78	97–98	72.34 (72.09)	6.58 (6.55)	21.09 (21.01)
IIIi	A	85	128–130	73.21 (73.24)	7.09 (7.10)	19.70 (19.60)

[a] Reported in Ref. [8].

(s, 3H, CH_3 at C6), 2.54 (s, 3H, CH_3 at C4). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ): 228.2 (CO_{trans}), 220.9 (CO_{trans}), 201.0 (CO_{cis}), 164.0 (C2), 160.1 (C6), 157.5 (C1′), 149.4 (C4), 130.8 (C4′), 128.6 (C3′ and C5′), 126.6 and 126.5 (C3 and C5), 122.7 (C2′ and C6′), 29.5 (C(6)CH_3), 20.7 (C(4)CH_3). ^{95}Mo-NMR: (CH_2Cl_2, δ) −1104.6 ($\Delta\nu_{1/2} = 29$ Hz). Cyclic voltammetry: (CH_2Cl_2, $^nBu_4NClO_4$ 0.1 M, 100 mV s^{-1}, V vs ferrocene): $E_a = 0.93$ V (0/+1), $E_{1/2} = -0.79$ V (0/−1, $\Delta E = 98$ mV), $E_{1/2} = -1.42$ V (−1/−2, $\Delta E = 156$ mV). Anal. Found: C, 48.54; H, 3.09; N, 10.01. $C_{17}H_{13}MoN_3O_4$ Calc.: C, 48.70; H, 3.13; N, 10.02%.

2.1.3. *cis*-Mo(CO)$_4$(L–L′) (**IV**) (L–L′ = **III**)

The synthetic method and the yield obtained for each complex are summarized in Table 2.

2.1.3.1. Method A. To a solution of 0.5–1.1 mmol of *cis*-(C_7H_8)Mo(CO)$_4$ in 50 ml of hexanes was added an equimolar amount of the ligand **III**, which was only slightly soluble. The mixture was stirred overnight, during which time complex **IV** precipitated from the solution. The solvent was removed, the solid residue was dissolved in CH_2Cl_2, and the resulting solution was filtered through Celite. Twice the volume of hexane was added to the filtrate, and the volume of the solution was reduced under vacuum, causing crystals of the product to precipitate. When it was judged that crystallization was complete, the remaining liquid was removed. The solid was washed with hexane and dried under vacuum.

2.1.3.2. Method B. Solid Mo(CO)$_6$ (1.00 mmol) was dissolved in 125 ml of tetrahydrofuran (THF) in a Pyrex immersion-type photolysis apparatus and irradiated at room temperature with a 450 W medium-pressure Hg lamp until the infrared spectrum of the solution showed that hexacarbonyl had been converted to *cis*-Mo(CO)$_4$(THF)$_2$. An equimolar amount of ligand **III** was added to the solution and, after 1 h of stirring, THF was removed under vacuum. The solid residue was washed with hexane, and then dissolved in CH_2Cl_2 and crystallized as described in method A. In the case of **IVe**, acetone was used in place of CH_2Cl_2 in order to obtain a crystalline product.

2.1.4. *cis*-Mo(CO)$_4$($H_2NHNC_5H_4N$) (**V**)

This compound was obtained by method A for the synthesis of **IV** but using 2-hydrazinopyridine, $H_2NHNC_5H_4N$, as the ligand. Commercial 2-hydrazinopyridine was dried under vacuum prior to use.

Table 2
Yields, melting points, and elemental analyses for *cis*-Mo(CO)$_4$(L–L′) complexes

Complex	Synthesis method	Yield (%)	Melting point [a] (°C)	Elemental analysis (Found (Calc.), %)		
				C	H	N
IVa [b]	B	31	91–92	42.56 (42.61)	3.03 (3.07)	9.02 (9.18)
IVb	A	73	128–130	47.19 (46.96)	3.22 (3.18)	10.32 (10.27)
IVc	A	58	86	45.82 (45.62)	2.82 (2.85)	10.69 (10.61)
IVe	B	30	96–98	38.16 (38.37)	2.14 (2.20)	8.90 (8.90)
IVg	B	35	94	47.19 (47.25)	3.22 (3.23)	10.32 (10.29)
IVh	B	56	103–105	47.19 (46.93)	3.22 (3.23)	10.32 (10.26)
IVi	B	24	70	47.99 (48.47)	3.64 (3.59)	9.84 (9.98)
V	A	63	148	34.09 (33.63)	2.23 (2.32)	13.25 (13.17)

[a] A single temperature indicates where decomposition appears to start.
[b] Isolated as the 0.5 CH_2Cl_2 solvate.

2.1.5. Oxidation of cis-$Mo(CO)_4(H_2NNHC_5H_4N)$ (**VI**)

The solid from a 0.55 mmol scale synthesis of *cis*-$Mo(CO)_4(H_2NHNC_5H_4N)$ (**V**) was dissolved in 100 ml of CH_2Cl_2, and the solution was cooled to 0 °C. Activated MnO_2 was added periodically over several hours, and the progress of the reaction was monitored by infrared spectrometry for the disappearance of the carbonyl bands of **V**. The reaction was complete in 5 h with a total addition of 300 mg of MnO_2. The solvent was removed under reduced pressure. The residue was dissolved in hexane at room temperature, and the solution was filtered through Celite. The volume of the filtrate was reduced under vacuum and the remaining solution was cooled to −78 °C. The cold solution was removed from the deep-blue crystals via cannula. The crystals were washed with cold hexane and then dried under vacuum to give 56 mg of solid.

3. Results and discussion

3.1. Syntheses

2-PHP ligands (**III**) are readily obtained in good-to-moderate yields by the reduction of corresponding 2-PAP (**I**). The synthesis of the complexes *cis*-$Mo(CO)_4(L–L')$ (L–L′ = **III**) (**IV**) by the reaction of poorly soluble ligand with *cis*-$Mo(CO)_4(C_7H_8)$ in hexane succeeded only for **IIIb** and **IIIc**, where the reaction was driven by the precipitation of the insoluble complexes **IVb** and **IVc**. Attempts to obtain complexes with other ligands by using a solvent such as CH_2Cl_2, in which the ligand **III** was soluble, failed because the reaction did not go to completion. Consequently, all the remaining complexes were obtained by the reaction of ligand with photochemically generated *cis*-$Mo(CO)_4(THF)_2$. Despite numerous attempts, complex **IVd** of 4-chloro-2-(phenylhydrazino)pyridine (**IIId**) was too unstable to be obtained in pure form. However, some of the spectroscopic data on this complex are provided in the appropriate tables.

No complex could be isolated for 5-trifluoromethyl-2-(phenylhydrazino)pyridine (**IIIf**). In addition to the methods used to obtain other complexes, the reaction of **IIIf** with *cis*-$Mo(CO)_4(CH_3CN)_2$ in CH_2Cl_2 and direct photolysis of **IIIf** and $Mo(CO)_6$ in CH_2Cl_2 or THF were tried. Although the infrared spectrum in the CO-stretching region of most reactions was consistent with the formation of some of the desired complex, the extent of reaction was small and no product could be isolated. The weak donor ability of the pyridyl nitrogen due to the strong electron-withdrawing ability of the CF_3 group apparently makes **IIIf** too weak a ligand to bind effectively.

The failure to obtain tetracarbonyl complexes for all the 2-PHP ligands indicates that the absence of the π-accepting azo group makes **III** poorer ligands than **I** for stabilizing zerovalent molybdenum complexes. Consistent with this is our inability to obtain complexes of the type *cis*-$Mo(CO)_2(L–L')_2$ and $Mo(L–L')_3$, which are well known for 2-PAP ligands [11].

All ligands (**III**) and their complexes (**IV**) are slowly oxidized in air, even as solids, to the corresponding 2-PAP ligand or complex, which is indicated by the yellow crystals turning orange or bluish-green, respectively. The ease of oxidizing **IV** to **II** was demonstrated by the addition of activated manganese dioxide to a solution of **IVb** in CH_2Cl_2 at room temperature, a procedure we have used to oxidize pentacarbonylchromium alkylhydrazine complexes to the azo complexes [12]. Oxidation was immediate and complete as evidenced by the change in color from yellow to deep blue and an infrared spectrum in the carbonyl-stretching region corresponding to *cis*-$Mo(CO)_4$(4-methyl-2-(phenylazo)pyridine) (**IIb**).

3.2. Infrared spectra

The carbonyl-stretching frequencies for **IV** are given in Table 3. The absence of the π-accepting azo group in 2-PHP ligands is evident in the considerably lower frequencies of **IV** compared with those of the corresponding 2-PAP complexes (**II**) [5]. However, **IV** shows the same trend of increasing carbonyl-stretching frequencies with increasing electron-withdrawing ability of

Table 3
Infrared and ^{95}Mo-NMR data for *cis*-$Mo(CO)_4(L–L')$ complexes of hydrazinopyridines

Complex	ν(CO) [a] (cm^{-1})	δ ^{95}Mo ($\Delta\nu_{1/2}$) [b] (ppm) (Hz)	σ_p/σ_m [c]
IVa	2020m, 1903s, 1875m, 1831m	−1130 (140)	−0.28
IVb	2020m, 1904s, 1875m, 1831m	−1125 (130)	−0.14
IVc	2020m, 1904s, 1877m, 1833m	−1121 (140)	0
IVd	2022m, 1906s, 1880m, 1835m	−1112 (190)	0.24
IVe	2023m, 1907s, 1881m, 1837m	−1105 (85)	0.37
IVg	2022m, 1905s, 1877m, 1831m	−1145 (150)	
IVh	2020m, 1904s, 1876m, 1833m	−1131 (140)	
IVi	2021m, 1904s, 1875m, 1829m	−1148 (155)	
V	2018m, 1899s, 1875m, 1829m	−1237 (65)	

[a] In CH_2Cl_2.
[b] In $(CD_3)_2CO$; uncertainties: δ, ±1 ppm; $\Delta\nu_{1/2}$, ±10 Hz.
[c] From Ref. [13].

Table 4
^{1}H-NMR assignment for 2-(phenylhydrazino)pyridines [a]

Compound	H3	H4	H5	H6	CH_3	H3′, H5′	H2′, H4′, H6′	NH [b]
IIIa	6.33d		6.29t	7.93d	3.94s	7.1–7.3m	6.8–6.9m	5.8s, 6.4s
IIIb	6.64s		6.52d	7.95d	2.20s	7.1–7.3m	6.8–6.9m	5.9s, 6.8s
IIIc	6.80d	7.43ddd	6.72ddd	8.13dm		7.1–7.3m	6.8–6.9m	5.8s, 6.3s
IIId	6.87d		6.70dd	7.97d		7.1–7.3m	6.8–6.9m	5.8s, 6.7s
IIIe	6.75d	7.55dd		8.15d		7.1–7.3m	6.8–6.9m	5.8s, 6.4s
IIIg	6.58/6.59d [c]	7.37t	6.58/6.59d [c]		2.40s	7.1–7.3m	6.8–6.9m	5.8s, 6.4s
IIIh	6.79dd	7.47dd	6.69ddd	8.10dm	2.24s	7.0–7.2m	6.7–6.9m [d]	5.8s, 7.0s
IIIi	6.44s		6.41s		2.15s, 2.33s	7.1–7.3m	6.8–6.9m	5.8s, 7.0s

[a] Recorded in $CDCl_3$. Chemical shifts are in ppm relative to tetramethylsilane.
[b] Peaks are broad.
[c] Either assignment may be correct.
[d] Does not include H2′.

the substituent on the pyridine ring as seen in **II**. For complexes **IVa**–**IVe**, there is a strong quantitative correlation ($r = 0.987$, $n = 5$) between the sum of the CO-stretching frequencies and the Hammett sigma parameter, a measure of the electron-withdrawing or -donating ability of the pyridyl substituent [13]. Therefore, the carbonyl frequencies are a good indicator of the electronic effect of the pyridyl substituents on the metal center.

3.3. NMR spectra

NMR spectral data for the ligands and complexes are summarized in Tables 3–7. The spectra for 2-PHP ligands **III** were taken in $CDCl_3$, while those for the complexes (**IV**) were recorded in DMSO-d_6, since they were not sufficiently soluble in chloroform and in acetone-d_6 the solvent sometimes obscured some of the CO signals in the ^{13}C spectrum.

In ^{1}H-NMR, the pyridyl protons of ligands (**III**) all shift downfield in the complexes (**IV**) but the shift order remains H6 > H4 > H3 > H5. This contrasts with 2-PAP ligands **I**, where coordination results in the chemical shift order H6 > H3 > H4 > H5 [5]. H3 proton is the one nearest to the phenylazo or phenylhydrazino substituent in the two ligands. Its significantly greater downfield shift, relative to other pyridyl protons in 2-PAP complexes (**II**), reflects the difference in electronic effects of the phenylazo group relative to the phenylhydrazino group. This difference also shows up in the shift of the C3 carbon. In 2-PAP ligands, the C3 carbon shifted downfield by 12–13 ppm upon coordination, while in 2-PHP ligands the shift is only 1–2 ppm, which is similar to all other carbons of the pyridyl ring. The identical chemical shifts of C2′ and C6′ and of C3′ and C5′ indicate free rotation of the phenyl group in both **III** and **IV**. This even appears to occur in **IVh** since the 4–4.5 ppm upfield chemical shifts of the C2′ and C6′ carbons compared with uncoordinated **IIIh** are similar to those in other 2-PHP ligands and complexes. This differs from the situation for 2-PAP ligands and complexes where the chemical shifts of the same carbon atoms suggested that complex **IIh** was unique in having restricted phenyl rotation.

2-PHP complexes (**IV**) show four signals for the carbonyl carbons, consistent with their unsymmetrical

Table 5
^{1}H-NMR assignment for *cis*-$Mo(CO)_4$(L–L′) complexes of hydrazinopyridines [a]

Compound	H3	H4	H5	H6	CH_3	H3′, H5′	H2′, H4′, H6′	NH [b]
IVa	6.63d		6.44dd	7.91d	3.82s	7.3–7.4m	7.0–7.1m	9.6s, 10.0s
IVb	6.65s		6.22dd	7.96d	2.26s	7.3–7.4m	7.0–7.1m	9.6s, 10.0s
IVc	6.85d	7.68ddd	6.75ddd	8.11d		7.3–7.4m	7.0–7.1m	9.7s, 10.0s
IVd [c]	6.85s		6.84d	8.07d		7.3–7.4m	7.0–7.1m	10.0s, 10.2s
IVe	6.80d	7.88dd		8.15d		7.3–7.4m	7.0–7.2m	10.0s, 10.2s
IVg	6.80d	7.58dd	6.73d		2.40s	7.3–7.4m	7.0–7.1m	9.6s, 10.0s
IVh	6.85d	7.69ddd	6.77ddd	8.15d	2.24s	6.9–7.3m	6.9–7.3m [d]	9.3s, 9.6s
IVi	6.65s		6.54s		2.08s, 2.22s	7.3–7.4m	7.0–7.1m	9.5s, 10.0s
V	6.63d	7.51ddd	6.57dd	8.07d				7.0s (NH_2), 9.0s (NH)

[a] Recorded in $(CD_3)_2SO$. Chemical shifts are in ppm relative to tetramethylsilane.
[b] Peaks are broad.
[c] From an impure sample.
[d] Does not include H2′.

Table 6
^{13}C-NMR assignment for 2-(phenylhydrazino)pyridines [a]

Compound	C2	C3	C4	C5	C6	C1′	C2′, C6′	C3′, C5′	C4′	CH_3
IIIa	162.5	90.3	167.8	103.5	148.9	148.1	112.4	129.2	120.2	54.9
IIIb	160.7	106.5	149.4	116.7	147.4	148.4	112.3	129.2	120.0	21.2
IIIc	160.4	106.2	138.2	115.3	147.9	148.1	112.3	129.3	120.2	
IIId	161.6	106.1	145.8	115.7	148.7	147.6	112.4	129.3	120.6	
IIIe	159.0	107.8	140.6	109.5	148.4	147.6	112.3	129.3	120.6	
IIIg	160.0	102.9	138.5	114.7	156.8	148.1	112.2	129.2	120.0	24.0
IIIh	160.5	106.2	138.2	115.1	147.8	145.7	121.5 (C2′), 111.0 (C6′)	127.1, 130.4 [b]	119.7	17.1
IIIi	160.5	103.3	148.9	116.0	156.4	148.4	112.2	129.2	119.8	21.1 (on C4) and 23.8 (on C6)

[a] Recorded in $CDCl_3$. Chemical shifts are in ppm relative to tetramethylsilane.
[b] Specific assignment of frequencies to C3′ and C5′ is uncertain.

structure. The two downfield signals for the *trans*-COs to the coordinated nitrogen atoms appear about 16 ppm downfield from the two signals for the *cis*-COs [14]. In contrast, the carbonyl carbon signals in 2-PAP complexes (**II**) were not observed due to fluxional broadening. The lone exception was complex **IIg**, where the steric effect of the 6-methyl substituent presumably slows the fluxional process. Even then, **IIg** gave only three carbonyl peaks. The 2-PAP ligands can adopt a planar configuration, allowing the two *cis*-COs in the complex to become equivalent, while this is not possible for the 2-PHP complexes. That the carbonyl carbon resonances are observed for *cis*-Mo(CO)$_4$(4,6-dimethyl-2-(phenylazo)pyridine) (**IVi**), newly synthesized as part of this work, and that there are only three signals are consistent with the earlier 2-PAP observations.

The complexes (**IV**) also were characterized by ^{95}Mo-NMR, which has become an important tool in the study of molybdenum compounds [15,16]. Interpretation of chemical shifts is generally based on the Ramsey equation ($\sigma = \sigma_d + \sigma_p$) which divides the total shielding (σ) into diamagnetic (σ_d) and paramagnetic (σ_p) contributions [17–20]. For heavy nuclei, such as ^{95}Mo, the paramagnetic term is the dominant factor influencing changes in nuclear shielding. For a series of compounds with the same symmetry, this paramagnetic shielding may be written as

$$\sigma_p = -K\ \Delta E^{-1} \langle r^{-3} \rangle_{4d} k^2,$$

in which K is a collection of constants and ΔE the average electronic excitation energy approximated by the HOMO-LUMO gap of the Mo d-orbitals. The radial term, $\langle r^{-3} \rangle_{4d}$, describes the average distance of the valence 4d electrons from the nucleus, while the factor k^2 describes their angular distribution. The last two terms are associated with the metal–ligand bond covalency, known as the nephelauxetic effect [15]. In general, the chemical shift moves downfield with decreased π- and/or σ-bonding and increased steric hindrance [15].

^{95}Mo-NMR data for 2-PHP complexes (**IV**) are given in Table 3. In each case, $\delta(^{95}\text{Mo})$ is shifted upfield from and the peak is broader than that of the corresponding 2-PAP complex [5]. Since the viscosity of acetone is lower than that of CH_2Cl_2, the solvent for the 2-PAP spectra, the larger linewidths for **IV** must be due to the change from the essentially planar 2-PAP ligand to the non-planar 2-PHP ligand [16]. The change in ligand from **II** to **IV** will affect all the terms in the equation for σ_p, and hence the direction of the chemical shift. While **III** lacks the π-bonding ability of **I**, the nitrogen atoms should be more basic, making **III** a stronger σ-donor. These two effects influence the chemical shift in opposite directions. There also is a change in steric effects suggested by the fluxional character of the CO ligands in **II** but not in **IV**. Finally, ΔE for **IV** must be larger than that for **II**, promoting an upfield shift. The 2-PAP complexes (**II**) showed a good correlation with a visible absorption band around 600 nm, suggesting the presence of an underlying ligand field band. The lowest energy band in **IV** appears at a much higher energy around 390–400 nm, although this does not appear to be a ligand field d–d transition and shows no correlation with $\delta(^{95}\text{Mo})$. However, several other correlations to $\delta(^{95}\text{Mo})$ of **IV** are observed.

The ^{95}Mo chemical shift of **IV** shows an excellent correlation ($r = 0.996$, $n = 5$) with the Hammett sigma parameter of the pyridyl substituent. In the series, $\delta(^{95}\text{Mo})$ shifts downfield as the pyridyl substituent becomes more electron-withdrawing. Since pyridines have been assessed as having negligible ability to act as π-acceptor ligands [21], this trend must be due to a decrease in σ-donor ability. Similar correlations with the pyridyl ring substituents were observed in the 2-PAP complexes [5] and the series of complexes Mo(CO)$_5$(py-R) [22] and *cis*-Mo(CO)$_4$(py-R)$_2$ [23], where py-R is a substituted pyridine.

Table 7
^{13}C-NMR assignment for *cis*-Mo(CO)$_4$(L–L′) complexes of hydrazinopyridines [a]

Compound	C2	C3	C4	C5	C6	C1′	C2′, C6′	C3′, C5′	C4′	CH_3	CO_{cis} [b]	CO_{trans} [b]
IVa	161.5	89.8	167.4	104.9	150.4	152.5	116.6	128.9	124.4	55.6	205.51, 207.37	221.26, 223.72
IVb	159.8	106.7	150.5	116.6	148.9	152.5	116.6	128.9	124.3	20.8	205.68, 207.50	221.36, 223.63
IVc	159.8	107.2	139.3	114.9	149.5	152.3	116.6	128.9	124.4		205.78, 207.53	221.38, 223.50
IVd [c]	160.4	106.1	144.7	115.2	150.7	151.9	116.6	129.0	124.6		205.54, 207.24	221.25, 223.25
IVe	158.8	108.9	141.6	107.0	148.5	152.0	116.7	129.0	124.6		205.57, 207.29	221.28, 223.17
IVg	160.6	104.4	138.7	115.2	157.8	152.4	116.7	128.9	124.4	28.5	205.27, 206.89	222.40, 223.20
IVh	160.1	107.5	139.6	116.5	149.3	145.7	125.2 (C2′), 114.9 (C6′)	126.8, 131.0 [d]	124.2	17.4	205.98, 207.20	220.95, 223.13
IVi	160.6	104.2	149.8	116.9	157.2	152.6	116.7	128.9	124.4	20.5 (on C4) and 28.2 (on C6)	205.19, 206.88	222.36, 223.31
V	160.0	107.1	138.4	113.6	149.4						207.65 [e]	221.49, 222.42

[a] Recorded in $(CD_3)_2SO$. Chemical shifts are in ppm relative to tetramethylsilane.
[b] For the CO signals *trans* and *cis* refer to the position of the CO relative to the L–L′ ligand.
[c] From an impure sample.
[d] Specific assignment of frequencies to C3′ and C5′ is uncertain.
[e] Intensity of this peak is ca. twice that of the two other CO carbons.

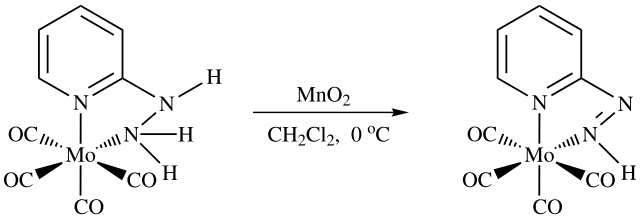
The molybdenum chemical shift also shows some correlation to the ^{13}C shift of the carbonyls of **IV**. Because L in *cis*-$M(CO)_4L_2$ affects the carbonyls *cis* and *trans* to it differently, these COs are treated separately in looking for correlations [24]. Also, because the nitrogen donor atoms in **IV** are not equivalent, we use the average of the chemical shifts for the *trans*- or *cis*-COs. A very good correlation ($r = 0.987$, $n = 7$) exists between $\delta(^{95}Mo)$ and $\delta(^{13}CO)$ for the *trans*-carbonyls provided that **IVh** is omitted. The ligand **IIh** is unique in having a substituent on the phenyl ring and so may have different steric effects. There is no correlation between $\delta(^{95}Mo)$ and the average *cis*-^{13}C CO shift or to the average of all ^{13}C CO shifts. The *cis*-$Mo(CO)_4(py\text{-}R)_2$ complexes gave good correlations with $\delta(^{95}Mo)$ for both the *cis*- and *trans*-^{13}C CO shifts, although the correlation with the *cis*-carbonyls was not as good as for the *trans* [23].The reason for the difference in the two cases is not clear but may be due to the non-planar ligands in **IV** affecting the *cis*-COs differently than the *trans*-COs. Given the correlation of $\delta(^{13}CO)$ for the *trans*-carbonyls to $\delta(^{95}Mo)$, it is not unexpected that $\delta(^{13}CO)$ also correlates well to the Hammett sigma parameter ($r = 0.960$, $n = 5$).

Since the Hammett sigma parameter correlates well with both the sum of the carbonyl-stretching frequencies and the molybdenum chemical shift, these two measures should correlate well with each other. Indeed, complexes **IVa**–**IVe**, for which a Hammett sigma parameter is defined, give an excellent correlation ($r = 0.990$, $n = 5$). The correlation is still good if complex **IVh** is added ($r = 0.949$, $n = 6$) but is poor if **IVg** and **IVi**, whose ligands have a 6-methyl group, are included. A similar pattern was noted in the 2-PAP complexes (**II**), although the adverse effect on the correlation is much greater for **IV**.

Finally, there is a strong correlation ($r = 0.978$, $n = 7$) between $\delta(^{95}Mo)$ for **IV** and $\delta(^{95}Mo)$ for **II** if complexes **IIh** and **IVh** are omitted. These are the only complexes in which the ligand has a substituent on the phenyl ring and so may create different steric effects. This would be consistent with the suggestion from the ^{13}C-NMR that there may be a difference in the ability of the phenyl group to undergo free rotation in **IIh** and **IVh**.

3.4. Complexes derived from 2-hydrazinopyridine

Synthesis of the 2-PHP complexes (**IV**) and their facile oxidation to the 2-PAP complexes stimulated us to undertake the synthesis of the analogous complexes of 2-hydrazinopyridine and 2-diazenopyridine. Complexes of 2-diazenopyridine have only recently been reported but none are known in which the metal center has a zero oxidation state [25–30].



V **VI**

The 2-hydrazinopyridine complex *cis*-$Mo(CO)_4(H_2NHNC_5H_4N)$ (**V**) is readily obtained in the same manner as the 2-PHP complexes (**IV**) and has similar physical and spectroscopic properties (Tables 3, 5 and 7). Addition of activated MnO_2 to a solution of **V** in CH_2Cl_2 results in an immediate color change from yellow to deep blue from which a dark blue solid was isolated. Unfortunately, slow decomposition of this solid, even at −25 °C, precluded obtaining a satisfactory elemental analysis. However, spectroscopic data are consistent with the formation of the (2-pyridyl)diazene complex *cis*-$Mo(CO)_4(HN{=}NC_5H_4N)$ (**VI**). The increased IR carbonyl-stretching frequencies in hexane of 2035m, 1959s, 1949m, and 1902m cm^{-1} are similar to those of the 2-PAP complexes (**II**) [5]. In the proton NMR in $CDCl_3$, the only signals present are ones attributable to the pyridyl protons plus a singlet at 14.69 ppm, which lies within the range found for the N=NH proton in known (2-pyridyl)diazene complexes [26,27,29,30].

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