Tetracarbonylmolybdenum complexes of 2-(phenylazo)pyridine ligands. Correlations of molybdenum-95 chemical shifts with electronic, infrared, and electrochemical properties

Martin N. Ackermann *, William G. Fairbrother, Neelim S. Amin, Charles J. Deodene, Carl M. Lamborg, Paul T. Martin

Oberlin College, Department of Chemistry, Oberlin OH 44074, USA

Abstract

The complexes cis-Mo(CO)$_4$(X-2-(phenylazo)pyridine) (X = 4-CH$_3$O, 4-CH$_3$, H, 4-Cl, 5-Br, 5-CF$_3$, 6-CH$_3$) and cis-Mo(CO)$_4$(2-(2-CH$_3$-phenylazo)pyridine) have been synthesized and characterized by cyclic voltammetry, by visible and infrared spectroscopy, and by ^{1}H, ^{13}C, and ^{95}Mo NMR spectroscopy. The ^{95}Mo chemical shift correlates with the lowest energy electronic transition, with the sum of the carbonyl stretching frequencies, with the first oxidation potential, and with Hammett σ parameters for the pyridyl substituents. The failure of the complexes cis-Mo(CO)$_4$(6-CH$_3$-2-(phenylazo)pyridine) and cis-Mo(CO)$_4$(2-(2-CH$_3$-phenylazo)pyridine) to fit some of the correlations is attributed to steric or electronic effects. The effect of a substituent on the pyridyl ring of 2-(phenylazo)pyridine appears to be entirely an inductive one operating through the σ bonding. It is suggested that the 2-(phenylazo)pyridines might be appropriately viewed as ligands whose strong π-acceptor ability resides with the azo group, while the pyridyl group acts primarily as a pyridine whose basicity has been decreased by the strong electron-withdrawing 2-phenylazo substituent.

Keywords: Molybdenum; Nuclear magnetic resonance; Pyridine complexes; Azo complexes; Electrochemistry

1. Introduction

Relative to other bidentate nitrogen-chelating ligands, 2-(phenylazo)pyridines, I, have been found to be effective at stabilizing transition metals in low oxidation states [1–6].
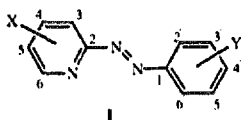
a X = 4-CH$_3$O, Y = H   e X = 5-Br, Y = H
b X = 4-CH$_3$, Y = H   f X = 5-CF$_3$, Y = H
c X = Y = H   g X = 6-CH$_3$, Y = H
d X = 4-Cl, Y = H   h X = H, Y = 2-CH$_3$

This ability is due to the presence of the azo group, which imparts a combination of strong π-accepting and weak σ-donating properties to the ligand. As part of our continuing interest in this ligand system, we have extended our earlier studies on the Group 6 carbonyl complexes of the parent ligand 2-PAP (Ic) to a variety of substituted 2-(phenylazo)pyridines, Ia–h, in order to explore the impact of electronic and steric effects on the properties of the resultant complexes. We also have chosen to focus on molybdenum complexes because of the ability to obtain ^{95}Mo NMR data, which has become an important tool for probing directly the metal center in such complexes [7,8]. In this paper we report on the monosubstituted complexes cis-Mo(CO)$_4$(L–L') (L – L' = Ia–h) and their characterization by infrared, NMR, UV–visible, and electrochemical methods.

2. Experimental details

2.1. General procedures

All reactions and measurements involving organometallic substances were carried out under a dry and

* Corresponding author. Tel.: (+1) 216 775 8066; fax: (+1) 216 775 8960; e-mail: martin@oberlin.edu.

oxygen-free atmosphere of nitrogen using standard Schlenk techniques. Solvents for those studies were purified by distillation under nitrogen; hexanes were distilled from CaH_2 and dichloromethane was distilled from P_4O_{10}. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. Infrared spectra were recorded on a Perkin–Elmer Model 1760 FTIR at 1 cm^{-1} resolution. Electronic spectra were recorded on a Cary 17 spectrophotometer. Melting points were taken on a Köfler hot-stage microscope and are uncorrected.

^{1}H and ^{13}C NMR spectra were obtained on an IBM/Bruker NR200 instrument at 200 and 50.3 MHz respectively. Generally, ^{1}H and ^{13}C NMR spectra of organometallic complexes were run in sealed tubes prepared on a vacuum line with $CDCl_3$ or CD_2Cl_2 that had been dried over P_4O_{10} and degassed by several freeze–thaw cycles. Chromium(III) acetylacetonate, Cr(acac)$_3$, at 0.07 M or less, was added to some samples for collection of ^{13}C spectra [9] with delay times of up to 10 s in attempts to detect the carbonyl carbons. ^{95}Mo NMR spectra were taken at 13.04 MHz at 1.0 Hz/pt resolution in 10 mm tubes prepared under a nitrogen atmosphere, using CH_2Cl_2 as solvent. Sample concentrations were in the range of 0.01–0.03 M. Spectra were recorded in the unlocked mode at 295 ± 1 °C using 2.0 M Na$_2$MoO$_4$ in D_2O (pH 11) as external standard and are accurate to ± 1 ppm. (Under these conditions Mo(CO)$_6$ in CH_2Cl_2 gave a shift of -1856 ppm.) An acquisition delay time of 200–1000 μs was used to minimize the effect of probe ringing on the spectral baseline.

Cyclic voltammetry was performed in a three-compartment cell using tetrabutylammonium fluoroborate as the supporting electrolyte and ferrocene as an internal standard, as previously described [6].

2.2. Reagents

4-Methyl-2-(phenylazo)pyridine (Ib) [10], 5-bromo-2-(phenylazo)pyridine (Ie) [10], 6-methyl-2-(phenylazo)pyridine (Ig) [10,11], 4-chloro-2-(phenylazo)pyridine (Id) [10,11], and 5-trifluoromethyl-2-(phenylazo)pyridine (If) [12] were synthesized according to the literature procedures, with the change that chromatography on alumina was done using petroleum ether–CH_2Cl_2 for elution, as described below for 4-methoxy-2-(phenylazo)pyridine (Ia). The complexes cis-Mo(CO)$_4$(2-PAP) (IIc) [6] and cis-(C$_7$H$_8$)Mo(CO)$_3$ (C$_7$H$_8$ = norbornadiene) [13] were prepared by the published procedures. Tetrabutylammonium fluoroborate (Southwestern Analytical Chemicals, Inc.) was dried overnight at 135 °C under vacuum before use. All other chemicals were used as obtained from commercial sources.

2.3. Syntheses

2.3.1. 4-Methoxy-2-(phenylazo)pyridine (Ia)

4-Chloro-2-pyridinamine was obtained from 4-chloropicolinic acid hydrazide, which was prepared from picolinic acid [14]. The hydrazide was converted to 4-chloro-2-pyridinamine by a modification of the method of Graf [15]. In our procedure the steam distillation was not performed. Instead, the solution from the treatment of the azide with acetic acid was made basic with 50% NaOH and then extracted with four 50 ml portions of diethyl ether. The ether was dried over K_2CO_3, the K_2CO_3 was removed by filtration, and the ether was removed under vacuum. Starting with 5.0 g of the hydrazide, 2.1 g (57%) of 4-chloro-2-pyridinamine was obtained.

4-Methoxy-2-pyridinamine was synthesized by modification of a literature procedure [16]. A sealed tube containing 3.0 g of 4-chloro-2-pyridinamine in a solution of sodium methoxide (made by dissolving 3.5 g of sodium in 45 ml of methanol) was heated at 145–150 °C for 7 h. The mixture was cooled, and the solvent was removed under vacuum. The solid residue was extracted seven times with 50 ml portions of diethyl ether, and the ether extracts were dried over K_2CO_3. The K_2CO_3 was removed by filtration, and the ether was removed under reduced pressure. Sublimation of the solid residue provided 1.7 g (58%) of white crystals of 4-methoxy-2-pyridinamine.

4-Methoxy-2-(phenylazo)pyridine (Ia) was prepared from 2.75 g (22.1 mmol) of 4-methoxy-2-pyridinamine and 3.0 g (28.0 mmol) of nitrosobenzene according to the general literature method for azopyridines [10]. The crude product was chromatographed on a 2.5 × 50 cm alumina column packed with petroleum ether. Development with petroleum ether–CH_2Cl_2 mixtures eluted minor yellow and orange bands at 5% and 50% CH_2Cl_2 respectively, and the major orange band of the desired product at up to 80% CH_2Cl_2. A dark orange-brown color remained at the top of the column. Removal of the solvent from the main fraction gave 2.90 g (13.6 mmol, 61%) of Ia with mp 40–42 °C. Anal. Found: C, 67.59; H, 5.20; N, 19.71. $C_{12}H_{11}N_3O$. Calc.: C, 67.43; H, 5.21; N, 19.65%.

2.3.2. 2-[(2-Methylphenyl)azo]pyridine (Ih)

2-[(2-Methylphenyl)azo]pyridine (Ih) was synthesized by reaction of 5.2 g (43.0 mmol) of 2-nitrosotoluene (Aldrich Chemical Co.) and 4.0 g (54.1 mmol) of 2-pyridinamine in the manner described for Ib [12]. However, a second chromatography was performed on the product, and the eluant was collected in fractions which were examined by TLC on silica gel using a 3:1 petroleum ether–CH_2Cl_2 solvent mixture. Pure frac-

Table 1
Yields, melting points, and elemental analyses for cis-Mo(CO)$_4$)L-L') complexes

Complex	Yield (%)	M.p. [a] (°C)	Elemental analysis (Found (Calc.) (%))		
			C	H	N
IIa	34	162	45.69 (45.62)	2.73 (2.63)	9.56 (9.98)
IIb	55	140	47.50 (47.45)	2.77 (2.74)	10.28 (10.37)
IId	63	168	42.41 (42.32)	1.93 (1.89)	9.79 (9.87)
IIe	70	132	38.45 (38.33)	1.77 (1.72)	8.91 (8.94)
IIf	71	123	41.89 (41.85)	1.82 (1.75)	9.18 (9.16)
IIg	60	143	47.33 (47.45)	2.72 (2.74)	10.30 (10.37)
IIh	25	120-122	47.57 (47.45)	2.76 (2.74)	10.31 (10.37)

[a] A single temperature indicates where decomposition appears to start.

tions were combined and the solvent was removed under vacuum leaving 2.91 g (14.8 mmol, 34%) of a dark red oil. Anal. Found: C, 72.98; H, 5.67; N, 21.27. $C_{12}H_{11}N_3$. Calc.: C, 73.08; H, 5.62; N, 21.30%.

2.3.3. Synthesis of cis-Mo(CO)$_4$(L-L') complexes (II)

A mixture of 1.14 mmol of cis-Mo(CO)$_4$(C$_7$H$_8$) and 1.14 mmol of L-L' (L-L' = Ia, Ib, Id-h) was stirred in 50 ml of hexanes at ambient temperature until the infrared spectrum in the carbonyl stretching region showed that reaction was complete (less than 24 h). The solvent was removed under reduced pressure and the residue was crystallized from hexanes-CH$_2$Cl$_2$ at −78 C. However, for IIa, IIb, and IIh purification was accomplished by chromatography instead of crystallization. The crude reaction mixture was applied to a 2 × 35 cm column of Florisil packed in petroleum ether, and the blue band of the complex was eluted with a 2:1 mixture of CH$_2$Cl$_2$-petroleum ether. Removal of the solvent yielded the analytically pure complex. The unoptimized yields and analytical data for all new complexes are reported in Table 1.

3. Results and discussion

3.1. Syntheses

The two new azopyridines Ia and Ih were obtained in the standard way [10] from the condensation of a 2-pyridinamine and a nitrosobenzene, each substituted as required. The complexes cis-Mo(CO)$_4$(L-L'), IIa-h, were readily synthesized from the reaction of cis-Mo(CO)$_4$(C$_7$H$_8$) with the appropriate ligand, Ia-h, in hexanes at room temperature. Only IIc has been reported previously [6].

3.2. Infrared and electronic spectra

The infrared spectra of the complexes in hexanes (Table 2) show the four carbonyl stretching bands expected for a cis-tetracarbonyl complex with octahedral

coordination except for IIh, for which the two middle bands are overlapped. Solutions of the complexes in hexanes are deep blue due to a strong absorption band ($\varepsilon \sim 10^4$) with λ_{max} around 600 nm. This band shifts slightly (less than 20 nm) to shorter wavelength in the more polar solvent dichloromethane. For a d^6 octahedral complex, the lowest energy electronic transition is from a filled metal d orbital to the unoccupied lowest energy π* orbital of the ligand(s), an MLCT transition [17]. The intensity of the observed band in IIa-h is consistent with an MLCT transition, although the modest solvent dependence of λ_{max} indicates that the polarity of the ground and excited states are similar [18].

3.3. Electrochemistry

The results of cyclic voltammetry in CH$_2$Cl$_2$ on IIa-h are summarized in Table 2. Each complex shows an irreversible oxidation and two reversible or quasi-reversible reductions. The potentials for the reduction of IIc are essentially identical with those previously reported in acetonitrile but the oxidation is 0.3 V more positive [6]. In keeping with the electronic structure of such d^6 complexes noted above [17], we take the oxidation to be from an orbital that is primarily metal-centered and the reductions to be to an orbital that is primarily of a ligand π* type. Consistent with this interpretation is the fact that the potential for oxidation increases as the substituent on the pyridyl ring of the ligand becomes more electron withdrawing while the potential for reduction becomes less negative. One measure of the electron-withdrawing or -donating ability of a substituent is its Hammett σ value. A plot of E_a vs. σ$_p$ or σ$_m$ values [19] for ligands Ia-f gives an excellent fit with a correlation coefficient r of 0.997 at a greater than 99.9% confidence level (C.L.) (based on a two-tailed t-test calculation) [20]. Since only the less reliable values of E_a instead of $E_{1/2}$ are available, the quality of this fit should not be over emphasized. However, it clearly establishes that a correlation exists. A similar plot for the first reduction potential also is good, with an r value of 0.943 (C.L. > 99.5%).

Table 2
Infrared, visible, ^{95}Mo NMR, and cyclic voltammetry data for cis-Mo(CO)$_4$(L-L') complexes

Complex	ν(CO) a (cm^{-1})	λmax (nm)		δ^{95}Mo (Δν$_{1/2}$) b		$E_{1/2}$ (V) c			σp/σm d
		Hexanes	CH$_2$Cl$_2$	(ppm)	(Hz)	+1/0 e	0/-1	-1/-2	
IIa	2025m, 1946s, 1934m, 1891m	619.1	604.0	-1042.6	(21)	0.88	-0.75	-1.40	-0.28
IIb	2026m, 1947s, 1935m, 1892m	617.1	601.8	-1046.2	(16)	0.90	-0.72	-1.37	-0.14
IIc	2027m, 1950s, 1938m, 1894m	615.5	603.0	-1030.4	(10) f	0.95	-0.72	-1.39	0
IId	2030m, 1955s, 1942m, 1899m	621.4	613.7	-984.7	(13)	1.01	-0.61	-1.32	0.24
IIe	2030m, 1955s, 1943m, 1900m	620.0	611.1	-991.6	(12)	1.04	-0.62	-1.30	0.37
IIf	2035m, 1962s, 1951m, 1907m	622.8	620.2	-929.7	(11)	1.07	-0.52	-1.21	0.46
IIg	2025m, 1944s, 1934m, 1891m	618.0	601.0	-1094.0	(24)	0.84	-0.74	-1.37	
IIh	2029m, 1949s, ~1943(sh), 1902m	583.2	577.6	-994.7	(12)	0.95	-0.83	-1.54	

a In hexanes. b In CH$_2$Cl$_2$. c Values vs. SCE in CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium tetrafluoroborate and a scan rate of 100 mV s^{-1}. d From Ref. [19]. e E_a values. f From Ref. [6].

When both the first oxidation and first reduction are one-electon processes, the difference in their potential, $\Delta E_{redox} = (E_{1/2}^{ox} - E_{1/2}^{red})$, can provide an assessment of the LUMO-HOMO gap. For a series of complexes this difference should correlate with the lowest energy electronic transition [21-24]. However, a plot of $1/\lambda_{max}$ from CH$_2$Cl$_2$ vs. ΔE_{redox} is poor for all complexes or for only the IIa-f subset. The uncertainty in having to use E_a^{ox} for $E_{1/2}^{ox}$ along with the very small range of ΔE_{redox} values (1.58-1.66 eV) may contribute to this failure.

3.4. NMR spectra

Assignments of the ^{1}H NMR spectra for all ligands and complexes (Table 3) were accomplished by analysis of coupling patterns and the effect of substituents on the pyridyl ring. The pattern of shifts for the pyridyl protons in all cases follows that originally noted for Ic and IIc [6]. In the ligands the order of chemical shifts is

$\delta_{H6} > \delta_{H4} > \delta_{H3} > \delta_{H5}$, while in the complexes it is $\delta_{H6} > \delta_{H3} > \delta_{H4} > \delta_{H5}$. All of the pyridyl protons are shifted downfield in the complex compared with the uncoordinated ligand with the magnitude of the change decreasing in the order H3 > H6 > H4 ~ H5.

Assignments of the ^{13}C NMR spectra of ligands and complexes (Table 4) were guided by DEPT spectra, by the pattern of substituent effects, and by the use of model compounds [25]. Proton coupled spectra were also run in some cases; even so, it was not possible to assign all of the phenyl carbons uniquely for Ih and IIh. The chemical shifts of the phenyl carbons in the ligands Ia-g differ by less than 1 ppm from those of trans-azobenzene [25]. The identical chemical shifts of C2' and C6' and of C3' and C5' in Ia-g and IIa-g indicate that there is free rotation of the phenyl ring in the uncoordinated ligands and in their complexes. The intensities of the peaks for these carbons also are about twice that of the next largest peak. Coordination of I to the Mo(CO)$_4$ moiety has only a small effect on most of

Table 3
^{1}H NMR assignment for ligands Ia-h and their complexes cis-Mo(CO)$_4$(L-L'), IIa-h a

Compound	H3	H4	H5	H6	CH$_3$	H2', H6'	H3', H4', H5'
Ia	7.34d		6.92dd	8.54d	3.92s	8.00-8.07m	7.49-7.56m
Ib	7.62ddqt		7.19ddqt	8.56ddqt	2.41s	7.99-8.05m	7.46-7.54m
Ic b	7.79ddd	7.87ddd	7.37ddd	8.71ddd		8.01-8.06m	7.49-7.55m
Id	7.81dd		7.39dd	8.63dd		8.00-8.07m	7.50-7.57m
Ie	7.72dd	8.01dd		8.78dd		7.97-8.05m	7.48-7.57m
If c	7.88dqt	8.12ddqt		8.98m		8.02-8.07m	7.51-7.58m
Ig	7.58dd	7.76dd	7.26dd		2.67s	8.00-8.07m	7.47-7.54m
Ih	7.6-7.9m	7.6-7.9m	7.2-7.4m	8.71dm	2.74s	7.6-7.9m d	7.2-7.4m
IIa	7.91d		6.99dd	8.82d	4.01s	7.90-8.01m	7.45-7.58m
IIb	8.25m		7.24dm	8.94d	2.59s	7.91-8.01m	7.46-7.57m
IIc b	8.42ddd	8.03ddd	7.42ddd	9.13ddd		7.94-8.00m	7.48-7.56m
IId	8.40dd		7.39dd	9.00dd		7.90-8.00m	7.47-7.62m
IIe	8.27dd	8.09dd		9.21dd		7.90-8.00m	7.45-7.57m
IIf	8.49dm	8.16dd		9.33m		7.93-8.00m	7.48-7.63m
IIg	8.22dm	7.92dd	7.44dd		2.97s	7.83-7.90m	7.50-7.58m
IIh	8.39dm	8.02ddd	7.43d	9.11dm	2.23s	7.3-7.5m d	7.3-7.5m

a Recorded in CDCl$_3$. Chemical shifts are in ppm relative to tetramethylsilane. b From Ref. [6]. c From Ref. [12]. d Does not include H2'.

Table 4
^{13}C NMR assignment for ligands Ia–h and their complexes cis-Mo(CO)$_3$(L–L'), IIa–h [a]

Compound	C2	C3	C4	C5	C6	C1'	C2', C6'	C3', C5'	C4'	Other
Ia	164.6	100.6	167.4	111.6	150.3	152.1	123.5	129.0	132.6	55.5 (CH$_3$)
Ib	162.9	116.2	149.7	126.1	149.1	152.3	123.4	129.0	131.9	21.1 (CH$_3$)
Ic	162.7	115.5	138.3	125.1	149.4	152.3	123.5	129.0	132.1	
Id	163.7	115.0	146.0	125.1	150.1	152.0	123.7	129.1	132.6	
Ie	161.2	116.2	140.8	122.3	150.5	152.1	123.6	129.1	132.4	
If [b]	164.6	114.4	127.5qt (3.4) [b]	127.5qt (33.4) [b]	146.6qt (4.0) [b]	152.1	123.8	129.2	132.9	123.1qt (CF$_3$) (272.5) [b]
Ig	162.6	110.6	138.3	124.8	158.4	152.2	123.4	128.9	131.9	24.3 (CH$_3$)
Ih	163.4	115.7	138.1	124.9	149.3	150.3	139.1 (C2') (112.94, 126.4, 132.1 (C4', C5', C6')) [c]	131.2 (C3')		17.5 (CH$_3$)
IIa	165.1	112.0	167.2	113.4	150.6	157.4	123.1	128.7	131.2	56.1 (CH$_3$)
IIb	163.6	128.6	149.7	126.3	149.5	157.4	123.1	128.7	131.1	21.1 (CH$_3$)
IIc	163.7	128.8	137.4	124.8	150.1	157.5	123.2	128.8	131.2	
IId	164.2	127.6	144.3	124.7	150.3	157.7	123.2	128.8	131.3	
IIe	162.3	128.3	139.9	121.2	150.2	157.6	123.2	128.8	131.2	
IIf	165.0	127.4	133.4qt (3.0) [b]	126.4qt (34.0) [b]	147.4qt (4.5) [b]	158.1	123.3	128.9	131.4	122.7qt (CF$_3$) (271.0) [b]
IIg	164.1	125.1	137.2	125.6	160.8	157.6	122.7	128.6	130.8	29.9 (CH$_3$), 200.6 (CO$_{cis}$) [d], 220.9 (CO$_{trans}$) [d], 228.4 (CO$_{trans}$) [d]
IIh	163.2	128.4	137.2	124.7	150.1	156.9	128.3 (C2') (123.3, 126.1, 127.6 (C4', C5', C6')) [c]	131.5 (C3')		17.6 (CH$_3$)

[a] Recorded in CDCl$_3$. Chemical shifts are in ppm relative to tetramethylsilane. [b] From Ref. [12]. [c] Numbers in parentheses are J_{CF} (Hz) for the quartet observed. [d] Specific assignment of frequencies to C4', C5', and C6' uncertain. [d] trans and cis refer to the position of the CO relative to the L–L' ligand.

the carbon chemical shifts, usually about 1 ppm or less, except for C3 and C1' which shift downfield by about 12–13 ppm and 5–6 ppm respectively. However, C2' in IIh is shifted upfield by 10.8 ppm from the uncoordinated ligand and at least one other carbon from among C4', C5', and C6' must shift at least 10 ppm downfield. This may be an indication of restricted rotation of the phenyl ring in this complex.
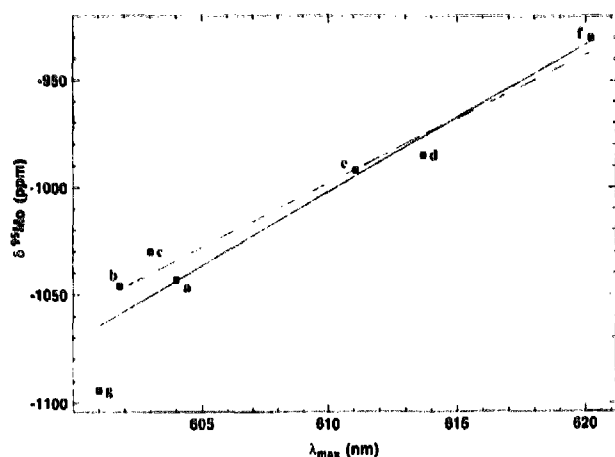

Fig. 1. Plot of λ_{max} in CH$_2$Cl$_2$ vs. $\delta(^{95}$Mo) for complexes IIa–g. The solid line is for all points (r = 0.953; C.L. > 99.9%). The dashed line excludes the point for IIg at the lower left (r = 0.984; C.L. > 99.9%).

Signals for the carbonyl carbons were observed only for IIg, and even then their low sensitivity required use of very long accumulation times (27 000 scans; 36 h). Even the more intense cis-carbonyl signal is only one-sixth as intense as the next strongest signal. Addition of the relaxation agent Cr(acac)$_3$ did not enhance their intensity [9,26], nor did it result in the appearance of carbonyl peaks for any of the other complexes. We propose that the absence of carbonyl peaks in all cases except IIg is due to fluxional behavior that broadens the carbonyl peaks at room temperature, whereas the methyl group in the 6-position of IIg sterically slows this process. Molybdenum tetracarbonyl complexes of α-di-imines are known to undergo cis–trans carbonyl exchange that is sensitive to the identity of the substituents [27]. Attempts to test this hypothesis by obtaining the spectrum of IIf at −40 °C showed no carbonyl peaks after 8 h, probably because of the low sensitivity of these signals. Thermal decomposition of the complexes precluded studies above room temperature.

Molybdenum-95 NMR has become an increasingly important tool in the study of molybdenum compounds [7,8]. Attempts to interpret NMR chemical shift trends generally are based on the Ramsay equation ($\sigma = \sigma_{dia}$ + σ_{para}), which divides the shielding σ into diamagnetic σ_{dia} and paramagnetic σ_{para} terms [7,8,28–31]. For heavy nuclei, such as ^{95}Mo, the paramagnetic term is

the dominant factor influencing changes in nuclear shielding and may be expressed as [32,33]

$$\sigma_{\text{para}} = \frac{-2e^2 h^2}{3m^2 c^2 \Delta E} \left[\langle r^{-3} \rangle_{np} P_\mu + \langle r^{-3} \rangle_{nd} D_\mu \right]$$

where np and nd refer to the valence p- and d-electrons respectively, P_μ and D_μ refer to the electron imbalance around the nucleus arising from the p and d electrons, and ΔE is the average electronic excitation energy. Sometimes ΔE can be taken simply as the lowest energy absorption. If the term in brackets, the nephelauxetic contribution, also is constant, then a linear correlation between the chemical shift and the wavelength of the lowest energy absorption can be observed within a series of related compounds [34,35]. Values of the ^{95}Mo NMR chemical shifts of the complexes IIa–h are given in Table 2. Fig. 1 shows a plot of $\delta(^{95}$Mo) vs. λ_{max} for IIa–g for data recorded in dichloromethane. As required by the σ_{para} expression, the shielding of the Mo nucleus decreases as λ_{max} (α $1/\Delta E$) increases. IIh is not included since it lies far off of any correlation, presumably because of effects arising from phenyl rather than pyridyl substitution. The importance of controlling steric and electronic factors in interpreting ^{95}Mo chemical shifts is well-documented [36]. The best line through all seven points in Fig. 1 yields a good correlation ($r = 0.954$; C.L. > 99.9%), suggesting that the term in brackets in the shielding equation is relatively constant for these complexes. The fit is even better ($r = 0.984$; C.L. > 99.9%) if IIg is excluded. The poorer fit of IIg may be further evidence for a steric effect of the 6-methyl group in this complex, as was suggested earlier by the ^{13}C NMR results. It is noteworthy that if λ_{max} values from hexane are used instead of those from dichloromethane, the correlation with $1/\Delta E$ is poor ($r = 0.760$). Thus, when possible, correlations should be drawn using data from the same solvent.

The ^{95}Mo chemical shifts also show a good correlation with the electron donor/acceptor ability of the pyridyl ring substituent. For complexes IIa–f this is manifested by a correlation coefficient of 0.915 (99.0% C.L.) for a plot of $\delta(^{95}$Mo) vs. the Hammett σ_p or σ_m values. Thus, the $\delta(^{95}$Mo) values reflect directly the electronic properties of the azopyridine ligands. A correlation with σ values has been reported in Mo(0) complexes for a series of substituted pyridine ligands in Mo(CO)$_5$L [37] and in cis-Mo(CO)$_4$L$_2$ [38] complexes (L = substituted pyridine) [37]. The ^{95}Mo chemical shift also correlates with the pyridine pK_a in the Mo(CO)$_5$L complexes and in the series of complexes cis-Mo(CO)$_4$(pip)$_{2-n}$L$_n$ ($n = 1,2$; L = substituted pyridine) [39]. Since only the pK_a of unsubstituted Ic has been reported [40], it is not possible to relate our data directly to the measured basicity of the azopyridine ligands. However, on the reasonable assumption that those ba-

sicities follow the Hammett σ values, as they do for the pyridines, our data are in accord with increased ligand basicity placing more electron density on the Mo atom to produce a more shielded environment, as in the pyridine studies. The sensitivity of $\delta(^{95}$Mo) to the substituents, as evidenced by the large range of shift values observed, is even greater in the case of the azopyridine ligands than for the pyridine ligands. Since the Hammett σ parameters correlate with E_a, it is not surprising that $\delta(^{95}$Mo) and E_a are also correlated. The full set of complexes IIa–h gives a correlation coefficient of 0.938 (C.L. > 99.9%).

The observation of excellent correlations of the cis-Mo(CO)$_4$L$_2$ complexes (L = 3- or 4-substituted pyridine) with Taft σ_I and σ_R parameters was interpreted to indicate that both inductive and resonance effects were important in the transmission of electron density from the pyridine substituents to the Mo center [38]. However, it also was noted that this provided no definitive information about the nature of the molybdenum–pyridine bond. In Mo(CO)$_5$L and cis-Mo(CO)$_4$(pip)$_{2-n}$L$_n$ complexes the correlation of $\delta(^{95}$Mo) with pyridine pK_a values was interpreted as being due only to the effect of the σ-donicity of the pyridine ligands [37,39]. This conclusion is in keeping with the fact that pyridines have negligible ability to act as π-acceptor ligands [41]. Likewise, the data for IIa–f suggest that the substitutent effects on the pyridyl ring of the 2-(phenylazo)pyridines are predominantly σ in character. The degree of π-acceptance of the 2-(phenylazo)pyridines due to the presence of the azo group [1,2,6] apparently is unaffected by the pyridyl substituents. This observation suggests that the 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
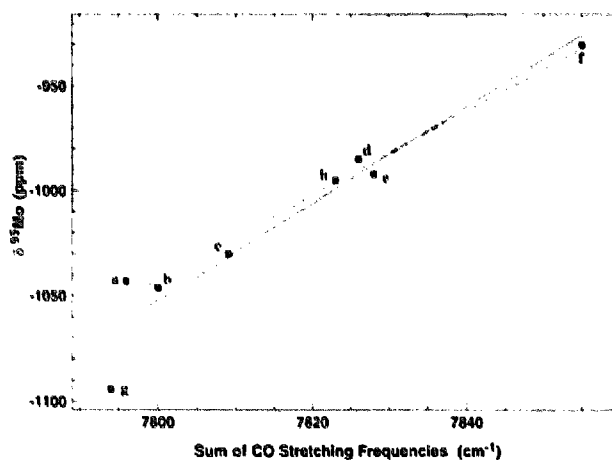

Fig. 2. Plot of the sum of the carbonyl stretching frequencies vs. $\delta(^{95}$Mo) for complexes IIa–h. The solid line is for all points ($r = 0.962$; C.L. > 99.9%). The dashed line excludes the point for IIg at the lower left ($r = 0.992$; C.L. > 99.9%).

decreased by the strong electron-withdrawing 2-phenyl-azo substitituent [42].

Some studies have noted a correlation between the ^{95}Mo chemical shift and the CO stretching frequencies or force constants in molybdenum carbonyl complexes [36–38,43]. An important consideration is that the steric effects of the series of ligands be the same. As all of the CO groups in the complex are affected by the other ligands, the use of the sum of all of the CO frequencies ($\Sigma\nu(C\equiv O)$), rather than a single frequency, has been proposed as a better approach to making these correlations [43]. For the complexes **IIa–h** a plot of $\delta(^{95}\text{Mo})$ vs. $\Sigma\nu(C\equiv O)$ (Fig. 2) gives a good fit ($r = 0.962$; C.L. > 99.9%) and demonstrates that the carbonyl frequencies provide a reliable measure of the electronic environment of the metal nucleus. Once again, **IIg**, in which the 6-methyl group may exert a steric effect, has the poorest fit in this correlation. If it is excluded, r increases to 0.992 (C.L. > 99.9%).

Since $\delta(^{95}\text{Mo})$ correlates both with the sum of the carbonyl frequencies and with E_a, it is not surprising that these two quantities also correlate with each other. With all eight complexes r is 0.939 (C.L. > 99.9%) and improves somewhat to 0.957 (C.L. > 99.9%) if the two complexes with possible steric (**IIg**) or different electronic effects (**IIh**) are excluded. This correlation between carbonyl frequencies or force constants and the first oxidation potential of a complex arises because both parameters, like $\delta(^{95}\text{Mo})$, are a measure of the electron richness at the metal center [44,45].

Acknowledgements

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