Synthesis and characterization of *cis*-Mo(CO)$_4$(L–L′) and *cis*-Mo(CO)$_2$(L–L′)$_2$ complexes of *N*(1)-methyl-2-(arylazo)imidazoles (L–L′). Correlations of spectroscopic data with substituent effects

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Abstract

N(1)-Methyl-2-(*p*-X-phenylazo)imidazoles (L–L′; X = CH$_3$O, CH$_3$, H, Br, CF$_3$, NO$_2$) react with *cis*-(norbornadiene)Mo(CO)$_4$ and Mo(CO)$_3$(CH$_3$CN)$_3$ to provide the complexes *cis*-Mo(CO)$_4$(L–L′) (X = CH$_3$O, CH$_3$, H, Br, CF$_3$, NO$_2$) and *cis*-Mo(CO)$_2$(L–L′)$_2$ (X = CH$_3$, H, Br, CF$_3$), respectively. The complexes were characterized by visible and infrared spectroscopy, by ^{1}H-, ^{13}C- and ^{95}Mo-NMR spectroscopy, and by cyclic voltammetry. Correlations among the data and correlations of the data with the Hammett sigma parameter within each set of complexes were investigated and are generally very good. These data, as well as the inability to synthesize complexes of the type Mo(L–L′)$_3$, indicate that 2-(arylazo)imidazoles are less effective ligands at stabilizing complexes of zerovalent metals than are 2-(arylazo)pyridines.
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1. Introduction

The strong π-acceptor ability of azoimines (−N=C−N=N−) makes them unusual among chelating nitrogen ligands in their ability to stabilize metals in their lower oxidation states. This was first recognized in the complexes of 2-(arylazo)pyridines with various metal ions [1–4]. Subsequent studies of azoimine complexes of copper(I) [5–7], osmium(II) [8–10], ruthenium(II) [11–14], and rhenium(II) [15–18] have demonstrated that the extent of this stabilization depends on the *N*-hetero-cyclic ring to which the arylazo linkage is attached. Based on electrochemical data the ability of an azoimine ligand to stabilize lower metal oxidation states increases in the order 2-(arylazo)imidazole < 2-(arylazo)pyridine < 2-(arylazo)pyrimidine.

2-(arylazo)imidazole   2-(arylazo)pyridine   2-(arylazo)pyrimidine
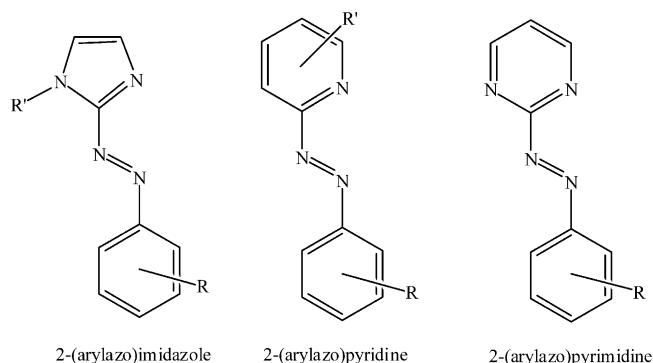
Our own work with azoimines has focused on zerovalent complexes of iron [19] and the Group 6 metals [20–22] and shows that azoimines also can have a significant effect on stabilizing complexes in which the metal is in a formally zero oxidation state. Thus, reaction of 2-(phenylazo)pyridine (2-PAP) with M(CO)$_6$ (M = Cr, Mo, W) yielded the series of complexes *cis*-M(CO)$_4$(2-PAP), *cis*-M(CO)$_2$(2-PAP)$_2$, and M(2-PAP)$_3$ [20]. The stability of the *cis*-M(CO)$_2$(2-PAP)$_2$, and M(2-PAP)$_3$ type complexes is unusual for complexes of chelating nitrogen ligands as is the ability

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to replace all six carbonyls by direct reaction of 2-PAP with M(CO)$_6$. Studies using molybdenum as the metal have demonstrated that the properties of these three types of complexes vary with the substituents on the pyridyl ring [21,22].

Given these results, we were interested in what effect replacing the pyridyl group with a different heterocycle would have on the types and properties of complexes obtained with zerovalent metals. Herein we report on our studies using $N(1)$-methyl-2-(arylazo)imidazoles (**I**) as the ligands. Since the studies with metal ions indicate that 2-(arylazo)imidazoles are the least effective at stabilizing lower metal oxidation states, it was expected that these azoimines might show a marked difference from the results using 2-(arylazo)pyridines. Our use of the $N(1)$ methylated ligand follows the lead of others in order to avoid possible reactivity at that nitrogen [5,6,10,12,14,15,18]. We also continue to use molybdenum as the metal because of the ability to probe directly the metal center in the complexes through ^{95}Mo-NMR.
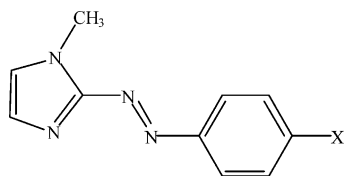
I

a X = CH$_3$O   **b** X = CH$_3$ **c** X = H
d X = Br   **e** X = CF$_3$ **f** X = NO$_2$

2. Experimental

2.1. General procedures

The general procedures for carrying out reactions, for handling air-sensitive materials, for purifying solvents, and for obtaining infrared, NMR, and cyclic voltammetry data have been described [20,21]. In addition, some of the NMR spectra were obtained on a 600 MHz system-^{95}Mo at 39.07 MHz, ^{13}C at 151 MHz, and HETCORR. Electronic spectra were recorded on a Cary 5E spectrophotometer. Melting points were taken in open capillaries and are uncorrected. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

2.2. Syntheses

2.2.1. Synthesis of N(1)-methyl-2-(arylazo)imidazoles (I)

The $N(1)$-methyl-2-(arylazo)imidazole ligands were prepared by methylation of the corresponding 2-(aryla-zo)imidazoles [23] as described in the literature [5]. The only major departure from the literature procedure was that the crude methylation product was not chromatographed. Instead, **If** was crystallized from an ethanol–water mixture and the others were crystallized from an acetone/hexane mixture.

$N(1)$-Methyl-2-(p-trifluoromethylphenylazo)imidazole (**Ie**) is a new compound and was prepared in a manner similar to the other ligands. The intermediate 2-(p-trifluoromethylphenylazo)imidazole, previously unreported, was prepared from p-trifluoromethylaniline in 56% yield on a 30 mmol scale. M.p. 204–205 °C. ^{1}H-NMR (CDCl$_3$, δ): 7.20 (s, 1H), 7.47 (s, 1H), 7.76 d, 2H), 8.02 (d, 2H). Treatment of 2-(p-trifluoromethylphenylazo)imidazole with methyl iodide in THF and recrystallization of the crude product from an acetone/hexane mixture gave **Ie** in 57% yield on a 33 mmole scale. For **Ie**: m. p. 119–121 °C. ^{1}H-NMR (CDCl$_3$, δ): 4.06 (s, 3H, CH$_3$), 7.19 (s, 1H, H5), 7.31 (s, 1H, H4), 7.74 (d, 2H, H8 and H10), 8.05 (d, 2H, H7 and H11). Anal. Found: C, 51.97; H, 3.67; N, 21.85. Calc. for C$_{11}$H$_9$F$_3$N$_4$: C, 51.97; H, 3.57; N, 22.04%.

2.2.2. cis-Mo(CO)$_4$(L–L') (II) (L–L' = I)

A mixture of 1.0 mmol of *cis*-(C$_7$H$_8$)Mo(CO)$_4$ (C$_7$H$_8$ = norbornadiene) [24] and 1.0 mmol of **I** were stirred in 50 ml of hexane (**Ia–d**) or CH$_2$Cl$_2$ (**Ie**, **If**) at room temperature (r.t.) until the infrared spectrum in the carbonyl stretching region showed the reaction was complete (1–2 days). The solvent was removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and filtered through a column of Celite. Hexane was added to the filtrate and the volume of the solution was reduced under vacuum, causing crystals of **II** to form. The remaining liquid was removed when it was judged that crystal formation was complete. The crystals were washed with hexane and dried under vacuum. The yield, melting point, and elemental analysis of the complexes are summarized in Table 1.

2.2.3. cis-Mo(CO)$_2$(L–L')$_2$ (III) (L–L' = I)

Molybdenum hexacarbonyl (1.0 mmol) was refluxed in 25 ml of CH$_3$CN until the infrared spectrum in the carbonyl stretching region showed complete conversion to Mo(CO)$_3$(CH$_3$CN)$_3$ [25]. The solvent was removed under vacuum and 30 ml of hexane and 2.0 mmole of **I** was added. The mixtures were refluxed for 16 h and then the solvent was removed under vacuum. The solid residue was crystallized as described for **II**. The yields, melting points, and elemental analyses of the complexes are summarized in Table 1.

Table 1
Yields, melting points, and elemental analyses for complexes *cis*-Mo(CO)$_4$(L–L') (**II**) and *cis*-Mo(CO)$_2$(L–L')$_2$ (**III**)

Compound	Yield (%)	M.p. [a] (°C)	Elemental analysis (Found (Calc.) (%))		
			C	H	N
IIa	79	165–166	42.36 (42.47)	2.83 (2.85)	13.28 (13.21)
IIb	78	160–162	43.97 (44.13)	3.00 (2.96)	13.62 (13.72)
IIc	61	119–121	42.62 (42.66)	2.60 (2.56)	14.26 (14.21)
IId	59	159–160	35.53 (35.54)	1.97 (1.92)	11.86 (11.84)
IIe	63	137–139	38.40 (38.98)	2.01 (1.96)	12.14 (12.12)
IIf	75	>270	38.29 (37.94)	2.07 (2.14)	15.95(15.78)
IIIb	43	~180	51.53 (52.18)	4.36 (4.38)	20.14 (20.28)
IIIc	65	~165	50.39 (50.16)	3.84 (3.87)	21.37 (21.25)
IIId	60	~205	38.74 (38.74)	2.72 (2.66)	16.25 (16.42)
IIIe	63	~145	43.40 (43.65)	2.92 (2.75)	16.79 (16.97)

[a] A single temperature indicates the compound undergoes decomposition that depends on the rate of heating. The temperature given is where melting/decomposition occurs immediately when the sample is placed in a preheated bath.

3. Results and discussion

3.1. Syntheses

The tetracarbonyl complexes *cis*-(CO)$_4$Mo(L–L') (**II**) were readily obtained for all ligands (**I**) from the reaction of the ligand with *cis*-(C$_7$H$_8$)Mo(CO)$_4$. However, reaction of **I** with Mo(CO)$_3$(CH$_3$CN)$_3$ only yielded complexes of the type *cis*-(CO)$_2$Mo(L–L')$_2$ (**III**) for **Ib-e**. Complex **IIIa** was observed but was too unstable to isolate in pure form, while no product could be detected for **If**. Attempts to obtain complexes of type **III**, *cis*-(CO)$_2$Mo(L–L')$_2$, and possibly even M(L–L')$_3$ by refluxing **I** and Mo(CO)$_6$ at a variety of temperatures, a successful approach using 2-(phenylazo)pyridine as the ligand [20], gave only intractable solid. In no case have we seen any evidence for a complex of the type M(L–L')$_3$ with the arylazoimidazoles (**I**).

The complexes **II** and **III** are slightly soluble in nonpolar solvents but reasonably soluble in polar solvents. Solutions of **II** in CH$_2$Cl$_2$ are blue or blue–green, while those of **III** are violet. For d^6 octahedral metal complexes the lowest energy electronic transition normally involves excitation of an electron from a filled metal d orbital to the lowest energy π* orbital of the ligand [26]. The intensity of the bands (ε ~10^4) is consistent with such a MLCT transition. Within each type of complex the wavelength of the visible absorption(s) generally increases as the electron-withdrawing ability of the phenyl substituent increases.

3.2. Infrared spectra

The tetracarbonyl complexes (**II**) show three bands in the infrared spectra in the carbonyl-stretching region. The expected fourth band appears only as a slight shoulder on the low frequency side of the second band.

In both **II** and **III** the carbonyl frequencies increase with the electron-withdrawing ability of the substituent on the phenyl ring of the ligand as was observed with the analogous 2-PAP complexes [21,22]. Both **II** and **III** show a strong correlation between the sum of the CO-stretching frequencies and the Hammett sigma parameter, a measure of the electron-withdrawing or -donating ability of the phenyl substituent [27]. For **II**, $r = 0.992$ ($n = 6$); for **III** $r = 0.978$ ($n = 4$). The data for **II** are plotted in Fig. 1. The sum of the frequencies is used since all of the COs are affected by the non-carbonyl ligand(s) [28]. The strong fit for the tetracarbonyl frequencies occurs even though only the three observed bands are used for the sum, presumably because the fourth band changes in the same direction and to the same extent as the others.
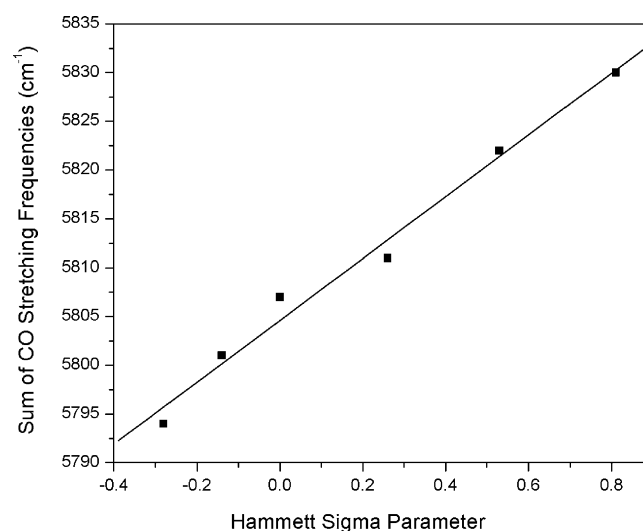

Fig. 1. Plot of the Hammett sigma parameter vs. the sum of the carbonyl stretching frequencies for type **II** complexes ($r = 0.992$).

3.3. Electrochemistry

The electrochemistry of complexes **II** and **III** in CH_2Cl_2 shows one irreversible oxidation and two reversible or quasi-reversible reductions. As with the 2-PAP complexes, we take the oxidation in these d^6 complexes to be from an orbital that is metal-centered and the reductions to be to a π^* ligand orbital [26]. This assignment is consistent with the effect of the phenyl substituent on the potentials. For both **II** and **III** the potentials for oxidation and reduction increase as the electron-withdrawing ability of the substituent increases. Attempts to draw correlations using the data for oxidation is of limited value since only E_a and not $E_{1/2}$ values are available. The correlation is poor for **II** ($r = 0.771$, $n = 6$) but good for **III** ($r = 0.960$, $n = 4$). However, the correlation between the first reduction, for which $E_{1/2}$ is available, and the Hammett sigma para-

meter is excellent with $r = 0.948$ ($n = 6$) for **II** and $r = 0.980$ ($n = 4$) for **III**.

3.4. NMR spectra

Proton and carbon NMR data for **II** and **III** are summarized in Tables 3 and 4. The carbon assignments were guided by the effect of the substituents on the phenyl ring, by HETCORR on some of the ligands, and by model compounds [29]. We attribute the absence of carbonyl carbon signals for the tetracarbonyl complexes (**II**) to fluxional behavior as occurs with the analogous 2-PAP complexes [21]. In the dicarbonyl complexes (**III**) the CO resonance shifts upfield as the electron-withdrawing ability of the phenyl substituent increases. This is consistent with the proposal that increasing π-acceptor ability of the non-carbonyl ligand should result in shielding of the CO carbon [30,31]. There is a good

Table 2
Infrared and ^{95}Mo-NMR data for complexes *cis*-Mo(CO)$_4$(L–L′) (**II**) and *cis*-Mo(CO)$_2$(L–L′)$_2$ (**III**) taken in CH_2Cl_2

Compound	ν(CO) (cm^{-1})	λ_{max} (nm)	δ ^{95}Mo ($\Delta\nu_{1/2}$) [a] (ppm) (Hz)	$E_{1/2}$ (V) [b]			σ_p [d]
				+1/0 [c]	0/−1	−1/−2	
IIa	2017m, 1925s, 1852m	596.3	−1119 (45)	0.79	−0.87	−1.82 [e]	−0.28
IIb	2018m, 1927s, 1856m	595.5	−1103 (27)	0.87	−0.89	−1.73	−0.14
IIc	2019m, 1929s, 1859m	594.4	−1090 (22)	0.86	−0.82	−1.62	0
IId	2020m, 1931s, 1860m	605.1	−1074 (27)	0.93	−0.78	−1.57	0.26
IIe	2022m, 1935s, 1865m	606.8	−1049 (24)	0.89	−0.72	−1.58 [e]	0.53
IIf	2022m, 1939s, 1869m	623.1	−1017 (21)	0.92	−0.53	−0.87	0.81
IIIb	1929s, 1858m	471.5, 561.4	324 (95)	0.26	−1.09	∼ −1.6	−0.14
IIIc	1933s, 1862m	471.3, 558.7	331 (107)	0.25	−1.09	−1.66 [e]	0
IIId	1934s, 1864m	475.4, 566.0	354 (130)	0.33	−1.01	−1.50	0.26
IIIe	1939s, 1869m	478.8, 564.8	392 (210)	0.37	−0.93	−1.34	0.53

[a] Uncertainty ±1 ppm.
[b] Values vs. SCE in CH_2Cl_2 with 0.1 M tetrabutylammonium tetrafluoroborate and a scan rate of 100 mV s^{-1}.
[c] E_a values.
[d] From Ref. [27].

Table 3
^{1}H-NMR assignment for complexes *cis*-Mo(CO)$_4$(L–L′) (**II**) and *cis*-Mo(CO)$_2$(L–L′)$_2$ (**III**) [a]

Compound	H4 [b]	H5 [b]	NCH$_3$	H8,H10 [b]	H7,H11 [b]	Other
IIa	7.47	7.26	4.06	6.98	8.15	3.90 (OCH$_3$)
IIb	7.50	7.29	4.08	7.28	7.96	2.44 (CH$_3$)
IIc	7.48	7.31	4.07	7.48	8.02	7.48 (H9)
IId	7.53	7.34	4.07	7.61	7.91	
IIe	7.56	7.38	4.09	7.75	8.07	
IIf [c]	7.62	7.48	4.08	8.35	8.13	
IIIb	6.78	6.57	3.84	7.19	7.47	2.38 (CH$_3$)
IIIc	6.80	6.60	3.83	7.3−7.6m	7.3−7.6m	7.3−7.6 (H9)
IIId	6.82	6.56	3.85	7.5m	7.5m	
IIIe	6.86	6.60	3.87	7.66s	7.66s	

[a] Recorded in CDCl$_3$. Chemical shifts are in ppm relative to tetramethylsilane.
[b] Doublet unless indicated otherwise.
[c] Recorded in CD$_2$Cl$_2$.

Table 4
^{13}C-NMR assignment for ligands (**I**) and complexes cis-Mo(CO)$_4$(L–L′) (**II**) and cis-Mo(CO)$_2$(L–L′)$_2$ (**III**) [a]

Compound	C2	C4	C5	C6	C7,C11	C8,C10	C9	NCH$_3$	Other
Ia	152.7	129.9	123.1	147.4	125.0	114.1	162.4	32.5	55.4 OCH$_3$
Ib	152.5	130.1	123.5	151.1	123.0	129.6	142.0	32.6	21.4 CCH$_3$
Ic	152.5 [b]	130.3	123.8	152.9 [b]	123.0	128.9	131.3	32.6	
Id	152.5	132.2	124.2	151.6	124.4	130.7	125.7	32.7	
Ie	152.4	131.0	124.8	154.6	123.0	126.1qt (3.9) [c]	132.1qt (32.5) [c]	32.7	123.7qt CF$_3$ (272.2) [c]
If	152.8	131.9	125.7	156.4	123.7 [d]	124.8 [d]	148.8	33.1	
IIa	157.0	129.8	125.0	150.9	124.7	113.8	162.6	33.8	55.6 OCH$_3$
IIb	157.2	129.7	125.2	155.0	122.8	129.3	141.8	33.9	21.3 CCH$_3$
IIc	157.3 [b]	129.8	125.5	156.9 [b]	122.9	128.7	130.8	34.0	
IId	157.5	129.7	125.0	155.8	124.3	131.8	125.6	31.5	
IIe	157.8	129.7	126.1	159.1	123.3	126.0qt (3.7) [c]	131.7qt (32.9) [c]	34.0	123.8qt CF$_3$ (272.2) [c]
IIf [e]	158.8	130.5	127.6	161.3	124.4 [d]	124.8 [d]	149.0	34.7	
IIIb	157.0	125.7	120.0	156.4	122.9	128.8	137.1	33.1	224.7 CO 21.0 CCH$_3$
IIIc	157.0	125.8	120.2	158.5	123.2	128.3	127.3	33.1	224.4 CO
IIId	157.0 [b]	125.9	120.5	157.2 [b]	124.7	131.3	120.9	33.1	224.3 CO
IIIe	157.0	126.1	120.8	160.5	123.6	125.6qt (3.8) [c]	129.0qt (32.6) [c]	33.2	224.2 CO 124.4qt CF$_3$ (271.8) [c]

[a] Recorded in CDCl$_3$.
[b] Assignments of C2 and C6 may be reversed.
[c] Number in parenthesis is J_{CF} (Hz) for the quartet.
[d] Assignments of C7,C11 and C8,C10 may be reversed.
[e] Recorded in CD$_2$Cl$_2$.

correlation of $\delta(^{13}CO)$ with the Hammett sigma parameter of the phenyl substituents ($r = 0.908$, $n = 4$) and with the sum of the CO stretching frequencies ($r = 0.942$, $n = 4$).

Although the cis-Mo(CO)$_2$(L–L′)$_2$ complexes (**III**) can exist in three isomeric forms (N and N′ refer to the imidazole and azo nitrogen atoms, respectively), the data and bonding considerations strongly support the cis/trans isomer. This structure is consistent with the equivalence of the two azoimidazole ligands indicated by the proton and carbon spectra and also optimizes π bonding between the metal and carbonyls by having the COs trans to an imidazole group rather than to the better π-accepting azo group. Additionally, the data and analysis parallel that for the analogous 2-PAP complexes, for which an X-ray crystal structure confirmed the cis/trans isomer [22].

trans/cis   cis/trans   cis/cis
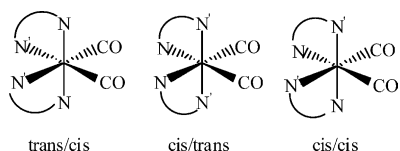
The Mo-95 NMR data for **II** and **III** are presented in Table 2. Molybdenum NMR has become a useful probe in the study of molybdenum compounds [32,33]. Interpretation of the chemical shifts is usually based on the

Ramsey equation ($\sigma = \sigma_d + \sigma_p$) where the total shielding is separated into diamagnetic (σ_d) and paramagnetic (σ_p) terms [34–37]. The paramagnetic term is dominant in heavy nuclei such as ^{95}Mo and is represented by the equation

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

for comparison of complexes with the same symmetry. Here K is a constant and ΔE, the spectrochemical parameter, is the average electronic energy approximated by the HOMO–LUMO gap of the Mo d orbitals. The radial term, $\langle r^{-3}\rangle_{4d}$, which is the average distance of the 4d electrons from the nucleus, and k^2, which describes their angular distribution, together comprise the nephelauxetic effect, which is associated with metal–ligand bond covalency [32]. The chemical shift generally moves downfield with decreased σ bonding and/or π bonding or increased steric hindrance.

The patterns of the ^{95}Mo chemical shifts for **II** and **III** are similar to those of the 2-PAP complexes [21,22]. The linewidths of **III** are larger than those of **II** due to the larger size of **III**. The increase of $\delta(^{95}Mo)$ from **II** to **III** is consistent with the ligands (**I**) being both poorer σ donors and poorer π acceptors than CO. The type **II** complexes show a very good correlation between $\delta(^{95}Mo)$ and λ_{max} ($\propto 1/\Delta E$) with $r = 0.932$ ($n = 6$). Such a correlation can arise in a series of complexes if

the nephelauxetic terms are constant and ΔE is taken as the lowest energy absorption [38,39]. However, in **II** the visible band involved is due to a MLCT transition and not a ligand field transition, which is the most important excitation in the Ramsey equation [40]. Hence, the observed correlation is either fortuitous or a ligand field band is coincident with the MLCT band.

The correlation of $\delta(^{95}\text{Mo})$ with the Hammett sigma parameter is excellent for both **II** and **III** with $r = 0.996$ in each case. Within each set of complexes $\delta(^{95}\text{Mo})$ shifts downfield as the electron-withdrawing ability of the phenyl substituent increases. Since $\Sigma\,\nu(\text{CO})$ correlates well with the Hammett sigma parameter, it is not surprising that $\delta(^{95}\text{Mo})$ and $\Sigma\nu(\text{CO})$ show a strong correlation. For **II** $r = 0.995$ ($n = 6$) and for **III** $r = 0.950$ ($n = 4$). These correlations indicate that the electronic effect of the phenyl substituents directly influences the metal center and that the carbonyl stretching frequencies are a good indicator of this electronic effect.

3.5. Conclusions

Overall, the correlations found among the data for **II** and **III** are better than those for the analogous 2-PAP complexes. This likely is due to the substituents in **I** all being at the same para position of the phenyl ring, while those in the 2-PAP ligands occur at both the meta and para positions of the pyridyl ring.

As noted above, studies on the complexes of azoimines with metal ions indicate that 2-(arylazo)imidazoles are not as effective as 2-(arylazo)pyridines at stabilizing metals in their lower oxidation states. The results reported herein, along with our previous work on 2-PAP complexes [21,22], show this also is the case for zeorvalent molybdenum complexes. Indications of this are evident in a qualitative way by the ready formation of 2-PAP complexes of the type $cis\text{-M(CO)}_2(\text{L}-\text{L}')_2$, and $\text{M(L}-\text{L}')_3$ simply by refluxing the ligand with Mo(CO)_6. By contrast refluxing **I** with Mo(CO)_6 gives no isolable products, and no evidence for the formation of a complex of the type $\text{M(L}-\text{L}')_3$ was obtained by any of the synthetic methods tried.

Quantitative indications of the greater ability of 2-(arylazo)pyridines to stabilize lower metal oxidation states can be seen in the carbonyl stretching frequencies and the first oxidation potential of the complexes. In order to eliminate differences in substituent effects, which appear through different rings of the two ligand types, it is best to compare complexes of the parent ligands 2-(phenylazo)pyridine and $N(1)$-methyl-2-(phenylazo)imidazole (**Ic**). The carbonyl frequencies of **IIc** and **IIIc** are significantly lower than those of the corresponding 2-PAP complexes cis-Mo(CO)$_4$(2-PAP) and cis-Mo(CO)$_2$(2-PAP)$_2$. Likewise, the first oxidation potentials of **IIc** and **IIIc** are 0.09 and 0.26 V lower, respectively, than those of the 2-PAP complexes [20].

Both types of data show that the molybdenum center is more electron rich in the $N(1)$-methyl-2-(phenylazo)imidazole complexes.

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