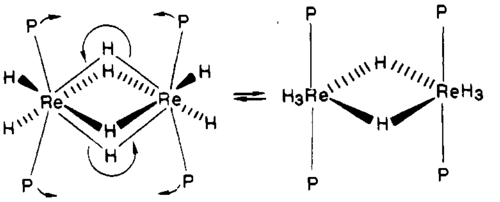
spectrum (CD_2Cl_2). This feature broadens with some loss in structure but is otherwise unchanged upon cooling to -70 °C.

We suggest that the structure of $Re_2H_8(dppm)_2$ can be considered to represent a distortion from $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ in which an opening up of the P–Re–P angles (constrained here to do so by the nature of the bridging dppm ligands), and a concomitant lengthening of the Re–Re bond is accompanied by a conversion of two of the bridging Re–H–Re units to terminal Re–H bonds. Such a low energy "concertina-like" process (see below) may well be the origin of the fluxionality of this class of molecule as a whole.



A final point of interest is the implication that the long Re–Re bond, coupled with the observed diamagnetism of the dppm complex, accords with the presence of a Re–Re single bond and, most likely, only a 16-electron count for the Re centers. Formally, at least, the dramatic Re–Re bond shortening that accompanies conversion to the $Re(\mu\text{-}H)_4Re$ structure is consistent with an 18-electron count and a Re≡Re bond. Further studies of the reaction and structural chemistry of these complexes are under way, especially those involving the dppe and dppm derivatives.

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Supplementary Material Available: Listing of atomic positional parameters, a figure showing the $Re_2(\mu\text{-}H)_2P_4$ core of $Re_2H_8(dppm)_2$ as viewed down the Re–Re bond axis, and a figure showing the ^{31}P 2DJ NMR spectrum of $Re_2H_8(dppm)_2$ (4 pages). Ordering information is given on any current masthead page.

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Articles

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Chromium, Molybdenum, and Tungsten Zerovalent Complexes of the Nitrogen Chelating Ligand 2-(Phenylazo)pyridine (2-PAP), Including Air-Stable *cis*-$M(CO)_2(2\text{-PAP})_2$ and $M(2\text{-PAP})_3$

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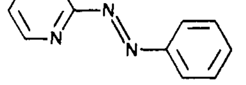
The reaction of 2-(phenylazo)pyridine (2-PAP) with $M(CO)_4$(norbornadiene), $M(CO)_3(CH_3CN)_3$, or $M(CO)_6$ provides $M(CO)_4(2\text{-PAP})$ (M = Cr, Mo, W), *cis*-$M(CO)_2(2\text{-PAP})_2$ (M = Mo, W), and $M(2\text{-PAP})_3$ (M = Cr, Mo, W) as air-stable solids. All compounds are diamagnetic except $Cr(2\text{-PAP})_3$, for which μ_{eff} is ~ 1.1 μ_B at ambient temperature. In $M(CO)_4(2\text{-PAP})$ and *cis*-$M(CO)_2(2\text{-PAP})_2$ the CO stretching frequencies are unusually high for complexes of a chelating nitrogen ligand. Compared to the frequency for uncoordinated 2-PAP, the N=N stretching frequency is lowered by 61–136 cm^{-1} in the complexes with the magnitude of the decrease following the order $M(CO)_4(2\text{-PAP}) >$ *cis*-$M(CO)_2(2\text{-PAP})_2 > M(2\text{-PAP})_3$. Cyclic voltammetry shows that the first oxidation occurs at relatively high potentials in these complexes. ^1H and ^{13}C NMR data suggest that the *cis*-$M(CO)_2(2\text{-PAP})_2$ and $M(2\text{-PAP})_3$ complexes may each exist in a single isomeric form. The ^{95}Mo chemical shifts increase by 900–1200 ppm for each pair of CO's replaced by 2-PAP in $Mo(CO)_6$; the shift of +1502 ppm for $Mo(2\text{-PAP})_3$ is over 1000 ppm more positive than any previously reported for a Mo(0) compound. The complexes are compared to those of other chelating nitrogen ligands. It is concluded that 2-PAP is a poor σ donor but a very good π acceptor toward low-valent metal centers.

Introduction

Reactions of diazenes (azo compounds) with metal carbonyls have provided a rich variety of complexes.[1] A simple but most often adopted mode of coordination of the diazene linkage is through σ donation by one of the nitrogen atoms to a metal center. In this mode diazenes also can participate in π bonding through use of the vacant N=N π^* molecular orbital. Evidence, such as lowering of the N=N stretching frequency upon coordination, indicates that simple diazenes have modest π-acceptor ability in low-oxidation-state metal complexes.[2]

As part of our continuing interest in diazenes as ligands, we were attracted to the chelating ligand 2-(phenylazo)pyridine (2-PAP). Because of reports that 2-PAP behaves as a strong π acceptor toward a variety of metal ions such as Ru(II),[3,4] Os(II),[5]



2-(phenylazo)pyridine, 2-PAP

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and Cu(I) and Cu(II),[6] it seemed likely that 2-PAP also might be a particularly effective π-acceptor ligand in low-valent organometallic systems. Furthermore, the chelating character should provide complexes that are more robust than those in which coordination occurs only through the diazene lone pair. In this paper we report our studies of the reaction of 2-PAP with the Cr, Mo, and W hexacarbonyls and related molecules.[7] The ease with which 2-PAP replaces all six carbonyl groups and the air-stability of the resultant tris complexes $M(2\text{-PAP})_3$ (M = Cr, Mo, W) are unprecedented for an α-diimine nitrogen chelating ligand and are an indication of the potentially novel chemistry that this ligand may engender in organometallic compounds.

Experimental Section

Procedures. All reactions were carried out under a dry and oxygen-free atmosphere of nitrogen by use of standard Schlenk techniques. Hexane and CH_3CN were distilled from CaH_2 under nitrogen; CH_2Cl_2 was distilled from P_4O_{10}. Tetrahydrofuran (THF) and diethyl ether were dried over sodium. These and other solvents were degassed by purging with nitrogen before use. Chromatography was performed using a 2 × 25 cm column of alumina or Florisil slurry-packed with petroleum ether.

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer Model 621 or 580B spectrometer. Magnetic susceptibility measurements were made at ambient temperature with a Johnson Matthey magnetic susceptibility balance. Melting points were taken in open capillaries or on a Kofler hot-stage microscope and are uncorrected.

Proton NMR spectra were obtained at 200 MHz on an IBM/Bruker NR200 instrument equipped with a broad-band probe. Carbon-13 spectra were taken at 50 MHz with a resolution of 0.4 Hz per point. Generally, samples for ^1H and ^{13}C NMR were prepared on a vacuum line with $CDCl_3$ that had been dried over P_4O_{10} and degassed by several freeze/thaw cycles. ^{95}Mo spectra were taken at 13.04 MHz in 10-mm tubes prepared under a nitrogen atmosphere, with 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 room temperature by using 2.0 M Na_2MoO_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, depending on the sample, to minimize the effect of probe ringing on the spectral base line.

Reagents. The compounds 2-PAP,[8] $Mo(CO)_4(bpy)$[9] (bpy = 2,2′-bipyridine), $C_7H_8M(CO)_3$[10] (C_7H_8 = norbornadiene; M = Cr,[10] Mo,[10] W[11]), *fac*-$(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W),[12] and $(CO)_3Cr(cht)$[10] (cht = 1,3,5-cycloheptatriene) were prepared by published procedures. Commercial $M(CO)_6$ (M = Cr, Mo, W) was sublimed before use. Tetrabutylammonium fluoborate (TBAF) (Southwestern Analytical Chemicals, Inc.) was dried overnight at 135 °C under vacuum before use. All other chemicals were used as obtained from commerical sources.

Electrochemistry. Cyclic voltammetry was performed using a Bioanalytical Systems CV-27 cyclic voltammograph and a Houston Instruments Model 100 X-Y recorder. The cell consisted of three compartments separated by glass frits. The working and counter electrodes were platinum wires, while a silver wire served as a pseudo reference electrode. Sample concentrations were between 7×10^{-4} and 3×10^{-3} M with 0.1 M TBAF as supporting electrolyte. Scan rates ranged from 25 to 800 mV/s. After the voltammograms of a sample were recorded, voltages were calibrated against the ferrocene/ferrocenium couple as internal standard by adding ferrocene and recording the voltammograms again.[13] For this couple $E_{1/2}$ was taken as 0.310 V vs SCE in CH_3CN[14] and 0.47 V vs SCE in CH_2Cl_2.[15] The reversibility of features was judged by the variation of ΔE_p and i_a/i_p with sweep rate and by comparison with these values for the known reversible ferrocene/ferrocenium couple.[14]

Preparation of $M(CO)_4(2\text{-PAP})$. Equimolar amounts (1–3 mmol) of $C_7H_8M(CO)_4$ (M = Cr, Mo, W) and 2-PAP were dissolved in 30 mL of hexane and stirred at ambient temperature until infrared monitoring of the carbonyl stretching region indicated that reaction had ceased. The solution was filtered, and the solid was washed with hexane until the washings were nearly colorless. The filtrate and washings were combined and cooled to −78 °C (sometimes after prior volume reduction). The resultant crystals were filtered cold, washed with cold hexane, and dried under vacuum. The reaction scale, reaction time, and yield were as follows: Cr, 3.10 mmol, 72 h, 712 mg (64%); Mo, 1.30 mmol, 17 h, 334 mg (65%); W, 1.00 mmol, 26 h, 223 mg (46%). The Mo and W products were analytically pure. Chromatography of the Cr complex on Florisil with elution using 2:5 CH_2Cl_2/petroleum ether gave an analytically pure product with substantial loss of material. Melting points (°C) for these blue to blue-purple compounds were as follows: Cr, 93–94; Mo, 107–110; W, 97–98. Anal. Calcd for $C_{15}H_9CrN_3O_4$: C, 51.88; H, 2.62; N, 12.10. Found: C, 52.09; H, 2.67; N, 12.17. Calcd for $C_{15}H_9MoN_3O_4$: C, 46.05; H, 2.32; N, 10.74. Found: C, 46.19; H, 2.40; N, 10.71. Calcd for $C_{15}H_9N_3O_4W$: C, 37.60: H, 1.90; N, 8.77. Found: C, 37.32; H, 1.97; N, 8.80.

Preparation of *cis*-$M(CO)_2(2\text{-PAP})_2$. M = Mo. A mixture of 566 mg (2.0 mmol) of $Mo(CO)_6$ and 320 mg (1.75 mmol) of 2-PAP was refluxed in 35 mL of *n*-octane for 45 min, during which time the initial red-orange solution turned to burgundy. The solution was stripped to dryness, the residue was taken up in a minimum amount of CH_2Cl_2, and the solution was filtered. Hexane was added, and the solution volume was reduced, causing preferential removal of the CH_2Cl_2 and precipitation of the product. The iridescent green crystals were filtered and washed with hexane to give 123 mg (0.24 mmol, 23%) of *cis*-$Mo(CO)_2(2\text{-PAP})_2$, mp 160–164 °C. The green color of the filtrate indicated the presence of $Mo(2\text{-PAP})_3$, but no attempt was made to isolate it. Although the sample appeared spectroscopically clean (NMR), good elemental analysis required chromatography on alumina with the purple band being eluted with a 1:1 CH_2Cl_2/petroleum ether mixture. Anal. Calcd for $C_{24}H_{18}MoN_6O_2$: C, 55.61; H, 3.50; N, 16.21. Found: C, 55.86; H, 3.86; N, 16.31.

M = W. A mixture of 322 mg (0.83 mmol) of *fac*-$W(CO)_3(CH_3CN)_3$ and 302 mg (1.65 mmol) of 2-PAP was refluxed in 25 mL of *n*-octane for 5 h. The burgundy solution was cooled and chromatographed on alumina. The purple band of the desired product was eluted with 7:3 CH_2Cl_2/petroleum ether, giving 117 mg (0.19 mmol, 23%) of analytically pure iridescent green *cis*-$W(CO)_2(2\text{-PAP})_2$, mp 162 °C dec. Anal. Calcd for $C_{24}H_{18}N_6O_2W$: C, 47.54; H, 3.00; N, 13.86. Found: C, 47.57; H, 3.04; N, 13.93.

Preparation of $M(2\text{-PAP})_3$. M = Cr. A mixture of 218 mg (1.00 mmol) of $Cr(CO)_6$ and 560 mg (3.00 mmol) of 2-PAP was refluxed in 25 mL of *n*-octane for 20 h. The solution was cooled, and the solid was collected by filtration. The crude product was taken up in a small amount of CH_2Cl_2 and filtered. After addition of 3 times the volume of petroleum ether, the solution was cooled to −30 °C, giving 286 mg (0.48 mmol, 48%) of very fine brown-black needles of analytically pure $Cr(2\text{-PAP})_3$, mp 198–200 °C. Similar yields of $Cr(2\text{-PAP})_3$ could be obtained by refluxing 2-PAP with *fac*-$(CH_3CN)_3Cr(CO)_3$ or $(CO)_3Cr(cht)$ in *n*-hexane. Anal. Calcd for $C_{33}H_{27}CrN_9$: C, 65.88; H, 4.53; N, 20.96. Found: C, 65.74; H, 4.51; N, 20.93.

M = Mo. A mixture of 215 mg (0.81 mmol) of $Mo(CO)_6$ and 550 mg (3.00 mmol) of 2-PAP was refluxed in 30 mL of *n*-octane for 7 h. Chromatography on Florisil gave four bands on elution as follows: (1) an unidentified yellow component with 3:7 CH_2Cl_2/petroleum ether; (2) a small amount of unreacted 2-PAP with 1:1:1 CH_2Cl_2/petroleum ether/diethyl ether; (3) a small amount of purple *cis*-$Mo(CO)_2(2\text{-PAP})_2$ with 4:1 diethyl ether/acetone; (4) green $Mo(2\text{-PAP})_3$ with 1:1 diethyl ether/acetone. Removing solvent from this last band, washing with petroleum ether, and drying gave 213 mg (0.33 mmol, 41%) of analytically pure black $Mo(2\text{-PAP})_3$, mp 174–176 °C. Anal. Calcd for $C_{33}H_{27}MoN_9$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.42; H, 4.24; N, 19.57.

M = W. A mixture of 463 mg (1.31 mmol) of $W(CO)_6$ and 963 mg (5.25 mmol) of 2-PAP was refluxed for 6 days in 30 mL of *n*-octane. After removal of solvent, the residue was taken up in CH_2Cl_2 and the

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solution was filtered. Five times the volume of hexane was added, the volume was reduced to remove CH_2Cl_2 preferentially, and the solution was cooled to −25 °C. Filtration gave 443 mg of crude black solid. A second reprecipitation gave 196 mg (0.27 mmol, 20%) of product that appeared pure in the NMR spectrum. However, analytically pure material was only obtained after chromatography on Florisil, the purple band of $W(2\text{-PAP})_3$ being eluted with 4:3 CH_2Cl_2/THF, and recrystallization from CH_2Cl_2/hexane. A large loss of product resulted in this process; e.g. 160 mg of initial product have only 34 mg of final material, mp 164 °C dec. Anal. Calcd for $C_{33}H_{27}N_9W$: C, 54.04; H, 3.71; N, 17.19. Found: C, 54.14; H, 3.71; N, 17.14.

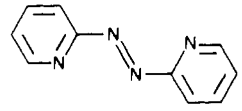
Preparation of *fac*-$M(CO)_3(PPh_3)(2\text{-PAP})$. A sample of $M(CO)_4(2\text{-PAP})$ and twice the molar quantity of PPh_3 were refluxed in 30 mL of *n*-hexane (M = Cr, Mo) or *n*-heptane (M = W) for 24 h. The cooled solution was filtered, and the crude product was washed with petroleum ether. Chromatography on Florisil gave a major blue or purple band, which was eluted with 1:1 CH_2Cl_2/petroleum ether. Crystallization from CH_2Cl_2/hexane gave dark purple crystals. The initial amounts of $M(CO)_4(2\text{-PAP})$, the recrystallized yields of $M(CO)_3(PPh_3)(2\text{-PAP})$, and the melting points were as follows: Cr, 1.71 mmol gave 380 mg (39%), mp 137–138 °C; Mo, 0.39 mmol gave 85 mg (35%), mp 165–166 °C; W, 0.21 mmol gave 19 mg (12%), mp 161–162 °C. Anal. Calcd for $C_{32}H_{24}CrN_3O_3P$: C, 65.92; H, 4.41; N, 7.21. Found: C, 66.07; H, 4.44; N, 7.17. Calcd for $C_{32}H_{24}MoN_3O_3P$: C, 61.44; H, 3.88; N, 6.72. Found: C, 61.60; H, 3.96; N, 6.80. Calcd for $C_{32}H_{24}N_3O_3PW$: C, 53.88; H, 3.38; N, 5.89. Found: C, 53.72; H, 3.40; N, 5.87.

Results and Discussion

Syntheses. With one exception the series of compounds $M(CO)_4(2\text{-PAP})$, *cis*-$M(CO)_2(2\text{-PAP})_2$, and $M(2\text{-PAP})_3$ (M = Cr, Mo, W) are readily obtained in fair-to-good yields from 2-PAP and an appropriate metal carbonyl precursor. The reaction of 2-PAP with $C_7H_8M(CO)_4$ at room temperature leads to $M(CO)_4(2\text{-PAP})$ for all three metals, although the yield of the Cr compound was low because of its lability. Likewise, the reaction of 2-PAP with $M(CO)_6$ (M = Cr, Mo, W) in refluxing *n*-octane (124 °C) for 1–6 days leads to complete replacement of all six CO ligands and formation of $M(2\text{-PAP})_3$. An attempt to reduce the reaction time for M = W by refluxing in tetralin gave primarily decomposition material. A shorter reflux time in *n*-octane gave a good yield of *cis*-$Mo(CO)_2(2\text{-PAP})_2$ but only a tiny yield of the analogous W complex and none of the Cr complex. Instead, *cis*-$W(CO)_2(2\text{-PAP})_2$ was obtained by using the more reactive precursor *fac*-$W(CO)_3(CH_3CN)_3$ and 2-PAP in boiling *n*-octane. However, our various attempts to obtain *cis*-$Cr(CO)_2(2\text{-PAP})_2$ all failed. At 25–40 °C the reaction of 2-PAP with $C_7H_8Cr(CO)_4$, $Cr(CO)_3(cht)$, or *fac*-$Cr(CO)_3(CH_3CN)_3$ gave only $Cr(CO)_4(2\text{-PAP})$, while at higher temperatures only $Cr(2\text{-PAP})_3$ was obtained.

All of these 2-PAP complexes are air-stable solids and give intensely colored solutions. While the $M(CO)_4(2\text{-PAP})$ compounds are soluble in polar and nonpolar solvents, the bis and tris 2-PAP compounds show appreciable solubility only in polar solvents.

Of the many chelating nitrogen ligands whose reactions with metal carbonyls have been studied, the closest analogue to 2-PAP is 2,2′-azobipyridine (abpy), which has the ability to coordinate to either one or two metal centers. Since the inception of our work,[7] group 6 metal complexes of the type $(abpy)M(CO)_4$ and $(abpy)[M(CO)_4]_2$ have been reported.[16] Like $Cr(CO)_4(2\text{-PAP})$, $Cr(CO)_4(abpy)$ is labile at room temperature.[16a] However, the failure to obtain $W(CO)_4(abpy)$ is surprising;[16a] our 2-PAP results suggest that it should be obtainable and stable. No attempts to synthesize bis or tris monometallic abpy complexes were reported.



2,2′-azobipyridine, abpy

Chart I

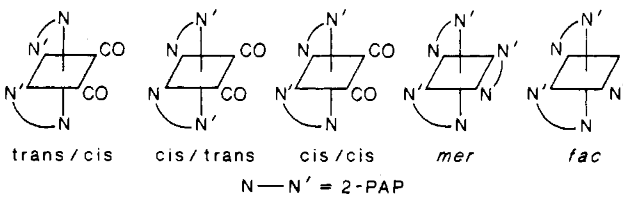


Table I. Carbonyl Stretching Frequencies for 2-PAP Complexes[a]

compd	$\nu(CO)$, cm^{-1}
$Cr(CO)_4(2\text{-PAP})$	2019 m, 1941 s, 1876 m
$Mo(CO)_4(2\text{-PAP})$	2026 m, 1938 s, ~1920 sh, 1868 m
$W(CO)_4(2\text{-PAP})$	2023 m, 1934 s, 1870 m
cis-$Mo(CO)_2(2\text{-PAP})_2$	1959 s, 1894 m
cis-$W(CO)_2(2\text{-PAP})_2$	1966 s, 1899 m
fac-$Cr(CO)_3(P(C_6H_5)_3)(2\text{-PAP})$	1955 vs, 1891 s, 1849 s
fac-$Mo(CO)_3(P(C_6H_5)_3)(2\text{-PAP})$	1953 vs, 1881 s, 1843 s
fac-$W(CO)_3(P(C_6H_5)_3)(2\text{-PAP})$	1958 vs, 1880 s, 1849 s

[a] Abbreviations: s, strong; m, medium; v, very; sh, shoulder.

Of the numerous other chelating nitrogen ligands whose reactions with metal carbonyls have been investigated, bis and tris analogues to our 2-PAP complexes have only been reported for the well-studied ligands 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). However, the conditions required to provide these compounds starting with the group 6 hexacarbonyls and bpy or phen as reactants were much harsher than those required for 2-PAP. Thus, $M(CO)_6$ (M = Cr) and bpy or phen (L-L) yield $Cr(L\text{-}L)_3$ when refluxed at 190 °C, but for M = Mo or W the reaction stops at *cis*-$M(CO)_2(L\text{-}L)_2$.[17] Instead, the Mo and W tris complexes were obtained by reduction of a metal salt in the presence of bpy or phen.[18] Furthermore, all of the bis and tris complexes of bpy and phen are extremely air-sensitive, even as solids. Finally, as with 2-PAP, the bis Cr complex could not be obtained directly; its synthesis was achieved by reaction of *cis*-$Cr(CO)_2((H_5C_6)_2PCH_2CH_2P(C_6H_5)_2)_2$ and L-L in liquid ammonia at 60 °C,[19] a reaction we have not attempted with 2-PAP.

Complete thermal replacement of all CO ligands in the group 6 hexacarbonyls to give zerovalent complexes cannot be accomplished with most ligands and usually is associated with strong π-acceptor ligands.[20] For chelating ligands, replacement of even four CO groups usually is not observed because of the stronger bonding experienced by a CO trans to a poorer π-acceptor than CO,[21] an effect that has long been recognized for nitrogen chelates such as bpy.[22] The radically different behavior demonstrated by 2-PAP in this regard is consistent with its earlier identification as a strong π-acceptor toward cations of Ru,[3,4] Os,[5] and Cu.[6]

Further reactions of the 2-PAP complexes with other ligands have involved only $P(C_6H_5)_3$ to date. Here reaction with $M(CO)_4(2\text{-PAP})$ provided good yields of *fac*-$M(CO)_3(2\text{-PAP})(P(C_6H_5)_3)$. No evidence for further substitution of CO by $P(C_6H_5)_3$ was found.

Since 2-PAP is an unsymmetrical ligand, there are three possible isomeric forms for *cis*-$M(CO)_2(2\text{-PAP})_2$ and two isomeric forms (*mer* and *fac*) for $M(2\text{-PAP})_3$ if a generally octahedral coordination sphere is assumed. These are shown in Chart I, where N and N′ refer to the pyridyl and azo nitrogens, respectively, and

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Table II. Carbonyl Stretching Frequencies and Force Constants for *cis*-$Mo(CO)_4$(L-L) Complexes

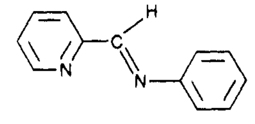
ligand	A_1	B_1	A_1	B_2	k_1	k_2	k_i
en[a]	2015	1890	1864	1818	13.76	15.25	0.42
bpy[a]	2017	1909	1878	1829	13.92	15.53	0.41
phen[b]	2018	1910	1881	1833	13.93	15.46	0.37
pmba[c]	2014	1915	1888	1842	14.04	15.48	0.34
2-PAP	2026	1938	~1920	1868	14.39	15.77	0.30
abpy[d]	2008	1942		1878	14.41	15.68	0.23

[a] Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533. [b] Hendricker, D. G.; Reed, T. E. *Inorg. Chem.* **1969**, *8*, 685. [c] pmba is *N*-(2-pyridinylmethylene)benzenamine, $(NC_5H_4)C(H){=}N{-}C_6H_5$: Brunner, H.; Herrmann, W. A. *Chem. Ber.* **1972**, *105*, 770. [d] Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

the geometry arrangements refer to the relative positions of N,N and N′,N′ in that order. Such isomers have been identified and isolated for several ruthenium and osmium bis and tris 2-PAP complexes.[3a,4c,e] However, we have observed no evidence of isomer separation during purification by either chromatography or crystallization.

Infrared Spectra. The carbonyl stretching frequencies of the 2-PAP complexes are presented in Table I. The number of bands and their intensity patterns are consistent with $M(CO)_2(2\text{-PAP})_2$ having a cis configuration and $M(CO)_3(P(C_6H_5)_3)(2\text{-PAP})$ being the *fac* isomer.

Comparison of the infrared data for the tetracarbonyls with those for other nitrogen chelate complexes is provided in Table II. Since Mo complexes have been the most widely synthesized, their values are used; data for Cr and W complexes, where available, are similar. Assignments for 2-PAP, abpy, and pmba are approximate since the complexes of these unsymmetrical ligands do not truly have C_{2v} symmetry. The force constants were obtained by using the Cotton–Kraihanzel method[23] and also assume C_{2v} symmetry. The complexes are listed in order of increasing values of the CO frequencies and force constants, which normally is taken to be the order of increasing π-acidity of the non-carbonyl ligand. By this criterion 2-PAP and abpy rank as the strongest π-acceptors in this series and are very similar.



N-(2-pyridinylmethylene)benzenamine, pmba

The CO stretching frequencies of a series of *cis*-$Mo(CO)_2$(L-L)$_2$ complexes also have been used to deduce the relative π-acceptor ability of chelating ligands L-L, giving an order of bpy < phen < dmpe < dppm < dppe < PF_3 (two PF_3 ligands take the place of one chelate).[24] Although 2-PAP is not a symmetrical ligand, it is not unreasonable to compare it with this series. On the basis of ν(CO) values the 2-PAP complex lies midway between the values of 1852 and 1786 cm^{-1} of dppe and 2040 and 2008 cm^{-1} of PF_3 and well above the frequencies of 1795 and 1728 cm^{-1} of phen, placing it high in π-acceptor ability.

The decrease in the N=N stretching frequency of coordinated 2-PAP compared to that of the free molecule also has been used as an indication of its strong π-acceptor property.[3-6] This interpretation is supported by X-ray structure results on $Ru(2\text{-PAP})_2(N_3)_2$,[25] $Ru(2\text{-PAP})_2Cl_2$,[26] and $Cr(2\text{-PAP})_2Cl_2$,[27] which show elongated N=N bonds and relatively short Ru—N(azo) or Cr—N(azo) bonds. Locating the N=N stretch in our complexes is relatively easy because it is quite intense and because it is the only feature to shift substantially relative to its location in the uncoordinated ligand. All other features in the 1300–1600-cm^{-1} region can be assigned to aromatic phenyl or 2-pyridyl modes.[6a] The extent of the decrease in ν(N=N) is considerable (Table III) and is comparable to that observed in other systems for which extensive π-back-bonding between the N=N group and the metal center has been demonstrated.[3-5] A decrease of ν(N=N) in Fe(II)[28] and Ni(0)[29] complexes of abpy also has been noted and related to metal–ligand π-bonding. That the stronger π-acidity of 2-PAP relative to α-diimines is due to the diazene group is evident by comparing 2-PAP with pmba. In $Mo(CO)_4$(pmba) ν(C=N) is lowered by only 56 cm^{-1} relative to the value in uncoordinated pmba.[30] The π*-acceptor orbital of the –N=N–group in 2-PAP has an energy lower than that of the –C(H)=N– group in pmba due to the more electronegative character of N compared to that of CH. Hence, the diazene group more readily accepts electron density when π-bonding to the metal. Hückel molecular orbital calculations revealed that abpy had the lowest LUMO among a number of nitrogen chelates and that the electron density in this LUMO is largely located at the diazene nitrogen atoms.[16a]

Table III. N=N Stretching Frequencies[a]

compd	ν(N=N), cm^{-1}	diff[b]
$Cr(CO)_4(2\text{-PAP})$	1288	128
$Mo(CO)_4(2\text{-PAP})$	1295	121
$W(CO)_4(2\text{-PAP})$	1280	136
cis-$Mo(CO)_2(2\text{-PAP})_2$	1316	100
cis-$W(CO)_2(2\text{-PAP})_2$	1326	90
$Cr(2\text{-PAP})_3$	1340	76
$Mo(2\text{-PAP})_3$	1340	76
$W(2\text{-PAP})_3$	1355	61
2-PAP	1416	

[a] Recorded in KBr pellet. [b] Frequency for uncoordinated 2-PAP minus frequency in the complex.

However, the effectiveness of a ligand is a function of both its π-acceptor and its σ-donor abilities.[31] In this regard 2-PAP is expected to be a poorer σ-donor than simple α-diimines such as bpy and phen. An approximate measure of σ-donor ability can be gained from the pK_a value of the conjugate acid of the ligand. The values for relevant systems are pK_a = 4.35 for bpyH$^+$,[32] pK_a = 2.0 for 2-PAPH$^+$,[33] and pK_a = −2.48 for azobenzeneH$^+$.[34] Thus, substitution of a pyridyl group in bpy with a phenylazo group lowers the basicity of the pyridyl group by over 2 orders of magnitude, while the diazene nitrogen, based on azobenzene, is over 6 orders of magnitude less basic than a bpy nitrogen. Graham concluded that pyridine is a slightly better σ-donor than CO,[35] while a more recent study ranks CO as significantly stronger than pyridine.[36] Hence, both 2-PAP nitrogens involved in coordination should be poorer σ-donors than CO. The poor σ-donor ability of 2-PAP is evident in Table III, where the difference between the coordinated and uncoordinated ν(N=N) values follows the order $M(CO)_4(2\text{-PAP})$ > *cis*-$M(CO)_2(2\text{-PAP})_2$ > $M(2\text{-PAP})_3$.

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Table IV. Proton NMR Assignments[a,b]

	pyridyl protons[c]				phenyl protons[d]		
complex	H-6	H-5	H-4	H-3	ortho	meta, para	$P(C_6H_5)_3$
2-PAP	8.71	7.37	7.87	7.79	8.01–8.06	7.49–7.55	
$Cr(CO)_4(2\text{-PAP})$	9.16	7.33	7.95	8.38	7.70–7.78	7.48–7.58	
$Mo(CO)_4(2\text{-PAP})$	9.13	7.42	8.03	8.42	7.94–8.00	7.48–7.56	
$W(CO)_4(2\text{-PAP})$	9.23	7.34	7.97	8.47	7.81–7.89	7.45–7.55	
$Mo(CO)_2(2\text{-PAP})_2$	7.41 d	6.63	7.54	8.01	7.55–7.65	7.35–7.50	
$W(CO)_2(2\text{-PAP})_2$	7.27	6.50	7.35–7.55 m	7.99	7.35–7.55		
$Cr(2\text{-PAP})_3$	paramagnetic, two broad features in region 5.5–8.5						
$Mo(2\text{-PAP})_3$	~7.5 m	6.54 m	~7.5 m	~7.5	5.94–6.01	7.05–7.10	
$W(2\text{-PAP})_3$	7.66 d	6.25	7.37	7.24 d	5.78–5.87	7.02–7.20	
$Cr(CO)_3(2\text{-PAP})(P(C_6H_5)_3)$	8.44 d	6.53 dd	7.4–7.5 m	7.92 d	7.4–7.5	7.3–7.4	6.9–7.3
$Mo(CO)_3(2\text{-PAP})(P(C_6H_5)_3)$	8.48 dm	6.73	7.50 dd	7.93 d	7.75–7.86	7.35–7.45	6.96–7.35
$W(CO)_3(2\text{-PAP})(P(C_6H_5)_3)$	8.40 d	6.53	6.9–7.7 m	7.96	6.9–7.7		6.9–7.7

[a] All assignments are in δ referenced to tetramethylsilane. [b] Abbreviations: d, doublet; m, multiplet. [c] Unless otherwise specified, all pyridyl proton signals are a doublet of doublet of doublets (ddd). Proton–proton coupling constants for the pyridyl protons could be obtained in most cases and fall in the following ranges: $J_{3,4} = 7.9–8.8$ Hz; $J_{3,5} = 1.0–1.4$ Hz; $J_{3,6} = 1.3–1.6$ Hz; $J_{4,5} = 6.5–7.3$ Hz; $J_{4,6} = 1.3–1.6$ Hz; $J_{5,6} = 5.5–6.3$ Hz. [d] All signals are complex multiplets.

Successive replacement of pairs of CO's by 2-PAP results in a less electron-rich metal through σ-donation and therefore less need for π-back-bonding to 2-PAP, despite the loss of the strongly π-accepting CO's.

NMR Data. The proton NMR data for 2-PAP and its complexes are summarized in Table IV. Assignment of individual pyridyl ring protons was aided by comparison with substituted 2-PAP ligands and their complexes.[37] The assignment for 2-PAP is in agreement with that previously proposed for the trans isomer.[38] For the most part the pyridyl protons shift slightly downfield in $M(CO)_4(2\text{-PAP})$ and then shift progressively upfield in $M(CO)_2(2\text{-PAP})_2$ and $M(2\text{-PAP})_3$. A downfield shift of the hydrogen atom ortho to the pyridyl nitrogen (H-6 in 2-PAP) has been observed for other chelating ligands containing a pyridyl group in their $M(CO)_4(L\text{-}L)$ complexes.[31b,39] The shifts of $M(CO)_4(2\text{-PAP})$ closely resemble those of the abpy analogue with $\delta_6 > \delta_3 > \delta_4 > \delta_5$, which is consistent with a nonplanar 2-PAP with a freely rotating phenyl group in the complex.[16a]

It was hoped that the NMR spectra might provide evidence for the presence of isomeric mixtures in the bis and tris compounds. In principle the inequivalence of the pyridyl group from one isomer to another should result in different proton chemical shifts in each complex. Also, in the cis/cis isomer of the bis complex the two pyridyl groups are inequivalent. For the tris complex the pyridyl groups are all equivalent in the *fac* isomer, while one 2-PAP differs from the other two in the *mer* isomer. However, none of the 2-PAP complexes exhibited more than one signal for any of the pyridyl protons. The complexes do not undergo exchange with uncoordinated 2-PAP, and the ^1H NMR spectrum of *cis*-$Mo(CO)_2(2\text{-PAP})_2$ did not reveal any spectral changes down to 215 K. Likewise, the ^{13}C spectra showed only a single resonance for each pyridyl carbon, and the two carbonyls of each bis complex gave only one resonance between them.

From these data it appears that either each complex exists as only a single isomer or the resonances in different isomers are too close to be resolved. Unfortunately the NMR spectra of the Ru(II) and Os(II) bis and tris 2-PAP complexes, which might serve as models, have not been reported.[3-5] The only NMR evidence for isomers in these systems is based on the shift of a meta CH_3 substituent on the phenyl ring.[3c,e,4] In a related system only one of the protons in the two different pyridyl groups of *cis*-$Mo(CO)_2(bpy)_2$ gave separate signals.[24] In the tris Ru(II) complex of the unsymmetric ligand 2-(2-pyridyl)thiazole the pyridyl protons of the *fac* and *mer* isomers were distinguishable, while two of the ring carbons exhibited resolvable shift differences both between isomers and within the *mer* isomer.[40] Since we would have detected differences as large as those found in these complexes, the implication is that each 2-PAP complex may consist of only a single isomer. For the tris complex this would be the *fac* isomer, which has the virtue of not placing the competing π-acceptor azo groups trans to one another. For the bis complex either the trans/cis or the cis/trans isomer is consistent with equivalent 2-PAP and CO ligands. In either case at least one pair of π-acceptors must be in a trans relationship. However, this effect would be less in the cis/trans isomer since each CO is trans to a pyridyl rather than to an azo group.

Chart II

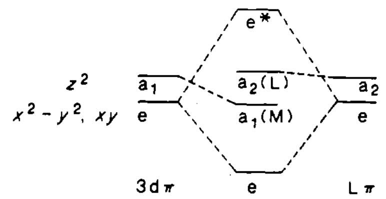

Table V. Molybdenum-95 NMR Shifts in CH_2Cl_2

complex	shift, ppm	$W_{1/2}$, Hz	ref
$Mo(CO)_6$	−1856	1	this work
$Mo(CO)_4(bpy)$	−1161	55	this work
$Mo(CO)_4(2\text{-PAP})$	−1030	10	this work
cis-$Mo(CO)_2(2\text{-PAP})_2$	+294	90	this work
$Mo(2\text{-PAP})_3$	+1502	180	this work
fac-$Mo(CO)_3(2\text{-PAP})(P(C_6H_5)_3)$	−763[d]	180	this work
$Mo(CO)_5(pyridine)$[a]	−1387	70	46
cis-$Mo(CO)_4(pyridine)_2$[b]	−1051	130	46
fac-$Mo(CO)_3(pyridine)_3$[b]	−800	7	46
$Mo(CO)_5(piperidine)$	−1433	80	46
cis-$Mo(CO)_4(piperidine)_2$[c]	−1093	90	46

[a] In $CDCl_3$. [b] In pyridine. [c] In dimethylformamide. [d] Doublet with $^1J_{Mo-P} = 150$ Hz.

The NMR spectrum of $Cr(2\text{-PAP})_3$ shows only two broad unresolved features even though TMS in the sample gives a sharp signal. Thus, the signal broadening must be due to paramagnetism within the complex and not to sample decomposition or to paramagnetic impurities. Magnetic susceptibility measurements on several different preparations of $Cr(2\text{-PAP})_3$, all with excellent elemental analyses, gave a value of about 1.1 μ_B for μ_{eff} for the solid. In this respect $Cr(2\text{-PAP})_3$ resembles the α-diimine complexes $Cr(phen)_3$ with a μ_{eff} value of 0.98 μ_B at room temperature[41] and $Cr(bpy)_3$ with a μ_{eff} value of 1.41 μ_B, which decreases with temperature.[42] A number of studies indicate that there is significant delocalization of electrons from Cr to bpy in $Cr(bpy)_3$, and the complex has been described by some as a Cr(III) complex

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Table VI. Electrochemical Data

compd	$E_{1/2}$, V[a]					
	+3/+2	+2/+1	+1/0	0/−1	−1/−2	−2/−3
Cr(CO)$_4$(2-PAP)			0.52	−0.85	−1.43 (i)	
Mo(CO)$_4$(2-PAP)			0.65 (E_a)	−0.72	−1.46 (q)	
W(CO)$_4$(2-PAP)			0.58 (E_a)	−0.68	−1.44 (q)	
Mo(CO)$_2$(2-PAP)$_2$			0.33 (E_a)	−0.97	−1.32	
Mo(CO)$_2$(2-PAP)$_2$[b]			0.51 (E_a)	−1.00	−1.31	
W(CO)$_2$(2-PAP)$_2$			0.39 (E_a)	−0.94	−1.25 (q)	
Cr(2-PAP)$_3$	1.05	0.50	−0.20	−1.10	−1.48	−1.7 (i)
Cr(2-PAP)$_3$[b]	1.29 (i)	0.68	−0.09	−1.11	−1.47	−1.75
Mo(2-PAP)$_3$[b]			0.24	−1.09	−1.76	
W(2-PAP)$_3$[b]			0.46 (E_a)	−1.04	−1.18	
2-PAP				−1.30		
2-PAP[b]				−1.26		
Cr(CO)$_4$(bpy)[c]			0.61			
Mo(CO)$_4$(bpy)[d]		1.08 (i)	0.52 (i)	−1.68		
W(CO)$_4$(bpy)[d]		1.02 (i)	0.53 (i)	−1.58		
Mo(CO)$_2$(bpy)$_2$[e]		0.30 (i)	−0.54	−1.64		
Cr(bpy)$_3$[f]	−0.21	−0.72	−1.28	−1.91	−2.26[g,h]	−2.45[g,h]
Mo(bpy)$_3$[i]	−0.01 (i)	−0.42	−1.13	−1.77	−2.15[h,j]	−2.9[h,j]
bpy[k]				−2.21	−2.46	

[a] Values vs SCE in CH_3CN with 0.1 M tetrabutylammonium tetrafluoraborate and a scan rate of 100 mV s^{-1} unless otherwise noted. i = irreversible; q = quasi-reversible. [b] In CH_2Cl_2. [c] With 0.075 M tetraethylammonium perchlorate at a scan rate of 50 mV s^{-1}: Lloyd, M. K.; McCleverty, J. A.; Orchard, D. G.; Connor, J. A.; Hall, M. B.; Hiller, I. H.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 1743. [d] With 0.1 M tetraethylammonium hexafluorophosphate at a scan rate of 500 mV s^{-1}: Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276. [e] Electrolyte and scan rate not specified: Chisholm, M. H.; Connor, J. A.; Huffman, J. C.; Kober, E. M.; Overton, C. *Inorg. Chem.* **1984**, *23*, 2298. [f] Referenced to Ag/AgCl, saturated NaCl electrode: Hughes, M. C.; Macero, D. J. *Inorg. Chem.* **1976**, *15*, 2040. [g] With 0.2 M tetrabutylammonium perchlorate in dimethylformamide. [h] Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *63*, 405. [i] In dimethylformamide; scan rate not given: DuBois, D. W.; Iwamoto, R. T.; Kleinberg, J. *Inorg. Chem.* **1970**, *9*, 968. [j] Polarography; 0.2 M tetrabutylammonium perchlorate in tetrahydrofuran. [k] With 0.1 M tetraethylammonium fluoborate: Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797.

of bpy$^-$.[43] A theoretical study of the bonding in M(bpy)$_3$ complexes concluded that the important molecular orbitals for these types of complexes in D_3 symmetry are of π character as shown in Chart II.[44] The a_1 and a_2 levels are close in energy, and their order may change with the metal and the net charge on the complex. Neutral complexes give the diamagnetic ground-state configuration $(e)^4(a_1)^2$ and an $^1A_1$ state. However, the $(e)^4(a_1)^1(a_2)^1$ $^3A_2$ state is thermally accessible, leading to the observed paramagnetism. Because 2-PAP is unsymmetrical, the symmetry of Cr(2-PAP)$_3$ will be lowered to C_3 (*fac*) or C_1 (*mer*) such that the a_1 and a_2 orbitals will have the same symmetry and can mix. Nonetheless, qualitatively the diagram will be similar and leads to a comparable interpretation for the origin of the paramagnetic character of Cr(2-PAP)$_3$. This diagram also has been applied to a series of Cr(quinone)$_3$ complexes, which have been similarly interpreted to be better formulated as Cr(III) semiquinone complexes.[45]

Recently there has been considerable interest in the use of ^{95}Mo NMR as a means of characterizing Mo compounds.[46] For the 2-PAP complexes the chemical shift (Table V) increases markedly with successive replacement of a pair of CO's by 2-PAP. Indeed, the value of +1502 ppm for Mo(2-PAP)$_3$ is the most positive chemical shift reported for a formally Mo(0) monometallic compound by over 1000 ppm. The next highest value we have found is +358 ppm for Mo(η^6-C_7H_8)$_2$.[47] Normally values for monometallic Mo(0) compounds lie in the range of 0 to −2000 ppm.[46] It appears that such large positive chemical shifts are associated with the addition of nitrogen atoms to the coordination sphere of the metal, rather than to 2-PAP itself. Thus, a similar effect occurs with bpy, pyridine, and piperidine as ligands (Table V), although data for more than two or three coordinated nitrogen atoms are unavailable in these cases. By comparison Mo(CO)$_3$(PR$_3$)$_3$ complexes (PR$_3$ = phosphine or phosphite) have shifts of −1500 ppm or lower.[46] This can be seen as well by the much smaller shift of Mo(CO)$_3$(2-PAP)(P(C_6H_5)$_3$) compared to that of Mo(CO)$_2$(2-PAP)$_2$. A comparable effect of coordinated nitrogen has been noted for Mo(II) complexes.[48]

Chemical shifts for ^{95}Mo are known to be sensitive to steric and electronic factors. The principal nuclear shielding effect is due to the paramagnetic component σ^p, but interpretation of measured shifts in terms of the theoretical expression has enjoyed limited success, particularly in cases where the types of complexes and ligands vary as much as with the above systems.[46] A full understanding of donor atom effects and their underlying origins also remains to be developed.[49] It will be of interest to examine other Mo(0) compounds with N-coordinated ligands, especially those with four or more coordinated nitrogen atoms.

Electrochemistry. The results of cyclic voltammetry experiments on the 2-PAP complexes are collected in Table VI. The limited solubility of M(2-PAP)$_3$ (M = Mo, W) in CH_3CN required use of CH_2Cl_2 as the solvent in those cases. All of the compounds show at least two reduction features and one or more oxidation features. By analogy with similar types of α-diimine complexes, we take the oxidations 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.[24,31a,b,50]

In every case the first reduction occurs at a more positive potential than in uncoordinated 2-PAP, reflecting the expected stabilization of the π^* MO upon coordination.[31a] For the tetracarbonyl complexes the first reduction potential follows the order W > Mo > Cr observed for other such α-diimine complexes.[31b,51] The closest analogous complexes should be those of abpy. For

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the Cr and Mo abpy tetracarbonyl complexes reduction is reported to occur at −0.55 V in DMF,[16a] which is estimated to be −0.65 to −0.75 V in CH_3CN when allowance is made for differences between the two solvents.[29b] Thus, the values are reasonably close to those for 2-PAP. ESR experiments and MO calculations on the anion of the bimetallic complex (μ-abpy)[$Mo(CO)_4]_2$ show conclusively that reduction places the added electron into a π^* abpy MO[16c] and strengthen the expectation that the same occurs in the monometallic complexes in abpy and 2-PAP.

For the 2-PAP tetracarbonyls only the Cr complex has a reversible first oxidation feature, while the Mo and W analogues offer only an anodic wave; the bis Mo and W complexes behave similarly. Such patterns are well-known in other α-diimine complexes, a consequence of the enhanced lability of the Mo(I) and W(I) species.[31a,b,50-52] If the Cr complex is scanned to more positive potentials, additional features are observed, but the return scan shows numerous unidentifiable features. Consequently, we do not cite values beyond the first oxidation.

The $M(2\text{-PAP})_3$ complexes present the most striking differences among the metals. The Cr complex exhibits the richest electrochemistry of any of our complexes. In CH_3CN it has three reversible oxidation features, two reversible reduction features, and one irreversible reduction feature. When CH_2Cl_2 is used as the solvent, six features are still evident but the third oxidation is irreversible. In addition, the third reduction is better defined, but the second reduction appears to be somewhat enhanced, probably due to overlap with the third reduction. The Mo and W compounds have only two reduction features and one oxidation feature, which for W is only the anodic wave. Scanning the Mo complex beyond the first reversible oxidation results in extensive decomposition.

The only other α-diimine for which the complete series of mono, bis, and tris complexes have been synthesized and studied electrochemically is bpy. Data for these complexes also are provided in Table VI. In general, the patterns for the bpy and 2-PAP complexes are similar, particularly the rich set of features for the Cr tris complex. In both cases the first reduction indicates that the π^* ligand orbital has been stabilized in all complexes, with the 2-PAP complex of a given type having a significantly more positive potential. This difference of 0.9–1.2 V is greatest for the tetracarbonyls but is still substantial at 0.7–0.9 V in the bis and tris complexes. The marked difference between the two ligands is evident from their effect on the stability of the highest occupied metal-centered orbital, as seen in the first oxidation. In the tetracarbonyl complexes the potential for this couple is essentially the same for both ligands.[53] Further replacement of CO's by the nitrogen chelate causes the potential of the couple to decrease, but much less so for 2-PAP than for bpy. Thus, in the case of Mo, for which values for all six compounds are available, the 2-PAP couple is 0.13, 0.87, and 1.37 V more positive for the mono, bis, and tris compounds, respectively. (The effect of solvent difference in the tris complexes will nearly cancel out since changing to CH_2Cl_2 or to DMF from CH_3CN increases the oxidation potentials by 0.1–0.2 V.) For Cr the mono and tris cases show a similar pattern. The greater ability of 2-PAP compared to that of bpy to stabilize lower metal oxidation states has been well-documented in the complexes of the metal ions Ru(II),[3,4] Os(II),[5] and Cu(I).[6] Ours is the first demonstration that this effect extends to formally zerovalent metal systems.

It has been argued that sufficiently poor σ-bonding ability by a ligand can effectively offset anticipated good π-accepting ability. Such was the conclusion for bipyrazyl compared to bpy from studies of their $Ru(L\text{-}L)_3^{2+}$ and $Mo(CO)_4(L\text{-}L)$ (M = Mo, W) complexes.[31a] Undoubtedly the π-acceptor ability of 2-PAP suffers some diminution due to its low σ-donor character (as inferred from its basicity), but the $\nu(N{=}N)$ infrared data clearly demonstrate that 2-PAP is involved in extensive π-bonding in all of the complexes presented here. Both σ- and π-effects have been found to be important in Ru(II) complexes of 2-PAP as well.[3a,31c]

The differences in the electrochemistry cited above between the bpy and the 2-PAP complexes can be understood in terms of the impact on the metal center as pairs of CO ligands are replaced by bpy or 2-PAP. The small difference in electrochemical behavior caused by variation of the metal centers in the tetracarbonyl complexes probably reflects the domination of the four remaining CO groups. However, as pairs of CO's are replaced by bpy, a π-acceptor much poorer than and a σ-donor comparable to CO, the metal center becomes increasingly more negative in character and less stable to oxidation. The stronger π-accepting and poorer σ-donating character of 2-PAP prevents such a negative charge accumulation on the metal and leads to a correspondingly more stable complex. It is just this "right balance" of π-acceptor and σ-donor abilities that makes 2-PAP unique as a nitrogen chelating ligand in its ability to replace all six CO's relatively easily to provide air-stable products. It will be of interest to investigate the reactions of 2-PAP with other zerovalent metal systems. Such studies, as well as work with substituted 2-PAP ligands, are in progress.

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Registry No. $C_7H_8Cr(CO)_4$, 12146-36-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $Cr(CO)_4(2\text{-PAP})$, 118275-50-6; $Mo(CO)_4(2\text{-PAP})$, 118275-51-7; $W(CO)_4(2\text{-PAP})$, 118275-52-8; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_2(2\text{-PAP})$, 118275-53-9; *fac*-$W(CO)_3(CH_3CN)_3$, 30958-95-3; $W(CO)_2(2\text{-PAP})$, 118275-54-0; $Cr(CO)_6$, 13007-92-6; $Cr(2\text{-PAP})_3$, 118275-55-1; *fac*-$(CH_3CN)_3Cr(CO)_3$, 22736-49-8; $(CO)_3Cr(cht)$, 12125-72-3; $Mo(2\text{-PAP})_3$, 118275-56-2; $W(CO)_6$, 14040-11-0; $W(2\text{-PAP})_3$, 118275-57-3; *fac*-$Cr(CO)_3(PPh_3)(2\text{-PAP})$, 118275-58-4; *fac*-$Mo(CO)_3(PPh_3)(2\text{-PAP})$, 118275-59-5; *fac*-$W(CO)_3(PPh_3)(2\text{-PAP})$, 118275-60-8; $Mo(CO)_4(bpy)$, 15668-64-1; ^{95}Mo, 14392-17-7; $Cr(CO)_4(2\text{-PAP})^+$, 118275-61-9; $Mo(CO)_4(2\text{-PAP})^+$, 118275-62-0; $W(CO)_4(2\text{-PAP})^+$, 118275-63-1; $Mo(CO)_2(2\text{-PAP})^+$, 118275-64-2; $W(CO)_2(2\text{-PAP})_2^+$, 118275-65-3; $Cr(2\text{-PAP})_3^{3+}$, 118275-66-4; $Cr(2\text{-PAP})_3^{2+}$, 118275-67-5; $Cr(2\text{-PAP})_3^+$, 118275-68-6; $Mo(2\text{-PAP})_3^+$, 118275-69-7; $W(2\text{-PAP})_3^+$, 118275-70-0; $Cr(CO)_4(2\text{-PAP})^-$, 118275-71-1; $Mo(CO)_4(2\text{-PAP})^-$, 118275-72-2; $W(CO)_4(2\text{-PAP})^-$, 118275-73-3; $Mo(CO)_2(2\text{-PAP})_2^-$, 118275-74-4; $Cr(2\text{-PAP})_3^-$, 118275-75-5; $Mo(2\text{-PAP})_3^-$, 118275-76-6; $W(2\text{-PAP})_3^-$, 118275-77-7; $Cr(CO)_4(2\text{-PAP})^{2-}$, 118275-78-8; $Mo(CO)_4(2\text{-PAP})^{2-}$, 118275-79-9; $W(CO)_4(2\text{-PAP})^{2-}$, 118275-80-2; $Mo(CO)_2(2\text{-PAP})_2^{2-}$, 118275-81-3; $W(CO)_2(2\text{-PAP})_2^{2-}$, 118275-82-4; $Cr(2\text{-PAP})_3^{2-}$, 118275-83-5; $Cr(2\text{-PAP})_3^{3-}$, 118275-84-6; $Mo(2\text{-PAP})_3^{2-}$, 118275-85-7; $W(2\text{-PAP})_3^{2-}$, 118275-86-8; $W(CO)_2(2\text{-PAP})_2^-$, 118275-87-9.

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